CROCKER NUCLEAR LABORATORY

University of California, Davis

Final Report
to the
California Air Resources Board
and
Project Clean Air
University of California, Riverside
on
Contract PCA-038

CYCLOTRON ANALYSIS OF ATMOSPHERIC CONTAMINANTS

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October 31, 1972

	ARB-R-PCA-038-19		PB-236 404/AS

Title and Subtitle
CYCLOTRON ANALYSIS OF ATMOSPHERIC CONTAMINANTS

5. Report Date
Oct. 31, 1972

6.

7. Author(s)
Thomas A. Cahill

8. Performing Organization Rept. No. UCD-CNL-162

9. Performing Organization Name and Address
Crocker Nuclear Laboratory
University of California, Davis
Davis, CA

10. Project/Task/Work Unit No.

11. Contract/Grant No.
PCA-038

12. Sponsoring Organization Name and Address
Air Resources Board
Resources Agency
1709-11th Street
Sacramento, CA. 95814

13. Type of Report & Period Covered
Final 6/30/71-9/30/72

14.

15. Supplementary Notes

16. Abstracts
This report summarizes the results of a one year effort to develop techniques to perform elemental analysis of atmospheric particulate samples using accelerator beams. The system is quantitative and absolute: every peak is compared directly to an elemental standard whose value is known to $\pm 7\%$. The system sensitivity for X-ray analysis ranges between about 10 and 100 ug/cm^2 for short runs, while values of about 10 ug/cm^2 are obtained for light elements in one hour via alpha scattering. The system analyses elements between sodium and uranium by X-rays, while elements between hydrogen and calcium (excluding Be) are analyzed by elastic alpha-scattering. The maximum through put per day is about 2400 X-ray analyses (fast); plus 24 X-ray analyses (slow); plus 96 alpha scattering analyses (light elements). Cost ranges between about $1.56/sample and about $10.00/sample for fast analysis, with the price for alpha scattering analysis set at about $20.00/sample when performed in tandem with fast analysis. The system is also applicable to other accelerators with heavy particle beams of 4 MEV/amu.

17. Key Words and Document Analysis.   17a. Descriptors
X-Ray analysis
Chemical analysis
X-Ray fluorescence
Alpha irradiation
Cyclotron
Air pollution
Aerosols

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

18. Availability Statement Release Unlimited
Available from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22151

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page
UNCLASSIFIED

21. No. of Pages
73

22. Price

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TABLE OF CONTENTS

INTRODUCTION

This report summarizes the results of a one year effort to develop techniques to perform elemental analysis of atmospheric particulate samples using accelerator beams.

Before going into the details of the system, the assumptions which have governed its development should be stated, and this seems to be as good a spot as any.

(1) Ideally, all elements present in a sample of the atmospheric aerosol should be detected.

(2) The sensitivity should be as good as possible.

(3) The system must be quantitative.

(4) The cost for an analysis must be low enough so that the system can be extensively used to improve data on air quality and identify pollution sources.

(5) The system should be able to use samples generated by presently used particulate collection systems on commonly used filter and impactor substrates.

(6) The analysis should be non-destructive.

(7) The system should be able to handle a large number of samples quickly.

In designing a system that attempts to fulfill these requirements for smog samples, one must keep in mind the characteristics of the sample. Elements lighter than calcium will generally make up the greater part of the aerosol mass, with significant amounts of mass in elements lighter than sodium. Many of these elements occur in chemically active forms that are injurious to living systems, so that information must be generated on these elements. If one plans to use x-ray analysis for elements sodium through calcium, which gives excellent sensitivity, one must keep the amount of material present to a minimum, or matrix effects will render the measurement non-quantitative. This requirement for light loadings then results in a stringent requirement for excellent sensitivity for these and other elements- especially toxic metals, but it does

simplify collection of an aerosol sample. One must also come up with some method for looking at elements lighter than sodium which (hopefully) is compatible with the x-ray analysis.

Another point is that although it is relatively easy to obtain an x-ray spectrum, it is difficult to identify elements correctly, subtract interferences, integrate peaks quantitatively and output data on the amount present in a useful form. If one is serious about performing elemental analysis of the large numbers of samples desired by air quality agencies, then one is led to the concept of a central analysis laboratory, either including a moderately large computer, or having access to such a computer.

An important consideration is that a system, once developed, should be able to be copied and duplicated within the state or around the country. One conclusion of this report is that any accelerator that can produce proton or heavier beams with a velocity of about 3×10^7 meters/ second can do such an analysis equally well. Almost 100 accelerators exist around the country that could be used for such analysis, so this consideration is easily met.

These considerations have resulted in the system summarized below. Each point will be treated in greater detail further in the report.

The UCD-ARB Aerosol Analysis System was designed and built at the
Crocker Nuclear Laboratory, University of California, Davis, under
Project Clean Air contract #PCA-038, to perform elemental analysis of
atmospheric contaminants. The system is designed to receive atmospheric
particulate samples on thin filter or impactor substrates. Elemental
analysis of the samples is performed using alpha particle induced x-rays
or elastically scattered alpha particles, with the Davis 76" isochronous
cyclotron serving as the source of the beams. Data is taken and reduced
by an integrated hardware-software system based on a PDP 15/40 computer
with CAMAC interfacing. Results are prepared on standard IBM-compatible
tapes and are printed out on the line printer and the hard-copy unit of
the interactive oscilloscope display.

This system has the following characteristics:

(1) It is quantitative and absolute, in that every peak is compared
directly to an elemental standard whose value is known to about $\pm$ 7%.
For routine analysis, especially for weak peaks, uncertainties in data
reduction codes presently do not allow the system to reach these levels
of accuracy.

(2) It has a broad range. Elements between sodium and uranium are
seen using x-rays, while elements between hydrogen and calcium (excluding
Be) are seen using elastic alpha-scattering. For elements lighter than
sodium, a special substrate must be used.

(3) It is sensitive. System sensitivity for x-ray analysis ranges
between about 10 and 100 ng/cm^2 for short runs ($<$ few minutes), while
values of about 10 $\mu g/cm^2$ are obtained for light elements in one hour
via alpha scattering. Using, for example, 1 mg/cm^2 mylar on a Lundgren
impactor, run at 4 cfm and 24-hour rotation speed, results in a value of
between 3 ng/m^3 and 10 ng/m^3 for elements sodium and above.

(4) It has a large capacity. The maximum throughput that can be
achieved in one day is presently about 2400 x-ray analyses-(fast)-plus
24 x-ray analyses-(slow)-plus 96 alpha scattering analyses (light elements).

This number converts to about 250,000 analyses/year within the present constraints, but it can be raised considerably by further tandem use of the beam.

(5) It has, generally, few corrections, the largest being self absorption. Self absorption corrections, calculated for a heavy atmospheric loading of 100 $\mu g/m^3$ of an urban character, and using a Lundgren impactor as mentioned in section (3), are about 14% for sodium, 10% for magnesium, 7% for aluminum, 5% for silican, and less for other elements. Thus, light loadings combined with high sensitivity result in reliable values under normal conditions.

(6) Sample handling is easy. Samples are mounted in standard 35 mm slide frames in Bell and Howell or universal linear slide trays.

(7) It has a low cost/sample. Cost ranges between about $1.50/ sample and about $10.00/sample for fast analysis, with the price for alpha-scattering analysis set at about $20.00/sample when performed in tandem with fast analysis.

(8) It has applicability to other accelerators. Any accelerator with heavy particle beams (protons or heavier) of about 4 MeV/amu ($\sim 3 \times 10^7$ m/sec) can perform this work equivalently well. Dozens of such accelerators are presently operational in the USA.

There are several negative factors concerning the system:

(1) Beam damage. Thick samples can be damaged or destroyed by beam heating, which limits the sensitivity that can be obtained. In addition, volatile elements may be lost unless special precautions are taken. These problems can be serious for some thick filters, but are less so for some thin filters and almost absent for thin plastic substrates. Steps are being taken to sharply reduce such effects.

(2) Vacuum effects. Loss of volatiles can occur because the analysis is carried out in a vacuum. Losses do not seem to be major for most components of smog, and can be minimized by spraying plastic over the samples before irradiation. (Less important than effect #1).

(3) Induced activity in the samples. This does not seem to be important, although activities of about 1.5 mr/hr. have been detected

after an intense irradiation of a heavily loaded filter sample.

(4) Turn-around time. Although the analysis is performed rapidly, present scheduling limits normal turn-around time for analysis to about one week. This can be shortened to one day if plans are firm a few weeks in advance.

(5) For heavily loaded samples, interference may reduce the sensitivity for certain elements by about a factor of 10 or more.

(6) The samples must be prepared on thin substrates, preferably about 1 mg/cm^2 mylar, Teflon, Kapton, polyethylene, or other such low-Z material.

A detailed summary of the comparison of this technique with other methods appears later in the report. However, a short summary is given here. The most closely competitive method to ion-induced x-ray analysis appears to be x-ray fluorescence using x-ray tubes or isotopic sources. Although each method has its advantages and disadvantages, both appear to result in dramatic increases in sensitivity to applications in which quantitative elemental analysis of microsamples are desired.

In the opinion of this report, ion-induced x-ray analysis is somewhat superior for analysis of samples in which quantitative information must be obtained on light elements (Na$\rightarrow$Ca) at the same time as heavy metals (Hg, Pb, etc.) for thin, lightly loaded samples on low-Z substrates. The ability of the UCD-ARB system to detect elements lighter than sodium adds another dimension to this system. It is thus suitable for a central analysis laboratory to handle routine monitoring, research and other such analyses in quantity.

X-ray fluorescence appears to have better sensitivity in some regions of x-ray energy, and can handle thick samples without damage, while in addition being able to give real time analysis in the field. It thus seems appropriate to fill the roll of a real-time analysis system for a moderate number of samples in a limited number of field locations.

One can envisage such a mix in California. Certainly, real-time x-ray fluorescence units could and should be located at several locations around the state that have severe aerosol problems, trained personnel, and computer facilities to support such a program. These facilities could

identify problems as they occur in a smog incident, as well as being used for detailed field studies of localized sources. Three such stations might require a capital outlay of about $105,000. This limited network would be combined with an extensive network of inexpensive, automatic remote units, generating samples that can be easily and cheaply analyzed by ion induced x-ray emission for a continuing record of air quality by particle size and elemental composition. A network of 60 such remote units might be set up for a capital outlay of around $75,000. These remote stations would give important information on the levels and types of aerosol experienced by the population at large, including respirable fractions, as well as giving reliable information on the sources of the aerosol, particularly when this information is combined with basic meteorological information.

The breakthroughs that have occurred in this field now provide the opportunity for the state and country to vastly improve the information available to air quality agencies at small cost.

BACKGROUND TO THE PROPOSAL

The atmospheric aerosol can be defined as the solid and liquid components of the atmosphere. These components, although generally present in amounts below 0.1 ppm, are important in a number of ways:

(1) They are a major cause of visibility limitation.

(2) They cause soiling.

(3) They are partly trapped out and retained by the lungs.

(4) They often contain heavy metals and other toxic substances.

(5) They can contain carcinogens.

However, unlike a gas which can be described in terms of two parameters—chemical specie and prevalance— the atmospheric aerosol consists of individual particles possessing an infinite variety of sizes, shapes, masses, liquid-solid mixtures and chemical compositions. Thus, in any attempt to characterize the aerosol, one must rely upon a variety of assumptions and approximations, although these can be buttressed a bit by spot studies of individual particles.

Given the inherent physical complexity of atmospheric particulates, it might seem foolish to also try to obtain chemical information on them. There are a number of reasons for doing this, however, especially when the problem at hand concerns pollution of the atmosphere.

(1) Since part of the aerosol is retained in the lung, it is important to know its chemistry so as to evaluate the health hazards associated with its inhalation. This information is thus vital to formulation of air quality standards for atmospheric particulates.

(2) Unlike gasses, the atmospheric aerosol often retains information on its sources in its chemical make-up. By this means, natural and anthropogenic contributions to the aerosol can be separated in many cases, and in fact, remarkably detailed information can be gained on the precise sources of the aerosol. This information, when combined with meteorological data, should enable air pollution agencies to bridge the gap between source inventories and air quality, and enable effective and efficient control strategies to be formulated.

The difficulties inherent in performing chemical analysis of air

samples are formidible, however. The small amount of material present
in the air generally demands pre-concentration by removing the aerosol
from the gaseous components of the atmosphere. To obtain a gram of
aerosol from a reasonably loaded air sample (120 μ/m^3 or about 0.1 ppm)
requires the efficient separation of this material from about 10,000 kgms
of air by mass (about 11 tons). Thus, a premium is placed on analysis
of microsamples of aerosol, since this greatly eases the problem of
aerosol collection.

Once one has obtained a sample, one is immediately struck by its
complicated chemical composition. While only a few elements are
responsible for most of the gaseous pollution of the atmosphere, an
aerosol sample can often contain 20 or more elements in various chem-
ical combinations. For the purpose of this report, the following
definitions will be made: very light elements, H $\rightarrow$ F; light elements,
Na $\rightarrow$ Ca; medium elements, rare earths and heavy elements. Also, since
many analyses techniques are destructive of the sample, the sample must
be further subdivided if a detailed study of its composition is to be
made.

These difficulties are sufficient to explain the lack of informa-
tion on the detailed chemistry of the atmospheric aerosol, despite the
importance of this type of knowledge. Several research studies have
been done,[1] despite these difficulties. However, the most advanced and
expensive analytical methods had to be used, thus limiting severely
the number of samples that could be characterized.

With the progress that was being made in x-ray techniques, several
possible ways appeared to greatly increase the sensitivity of elemental
analysis for atmospheric aerosol samples. This would still not answer
uniquely the question of the chemical form of the aerosol, but it would
be a step in the right directions. After consultation with many experts
in the field of atmospheric pollution, a number of criteria was drawn up
that should ideally be met by a system for the analysis of atmospheric
aerosol samples: the techniques should have good sensitivity- as good as
possible, and should certainly be an order of magnitude better than any
existing or contemplated elemental standard; the method should be broad-
ranged and non-selective. Ideally, all components of the aerosol should

be observed. Since much of the mass of an urban aerosol will consist of elements lighter than sodium, this will pose a problem for x-ray based methods. The system must also be quantitative, absolute and thus reproducible, and should result in a low cost/sample, so that it could be widely used.

Any method that can even partially meet this criterion will already be an improvement over any existing method, but, in addition, the method should be: non-destructive; fast, in turn-around time between sample collection and data output; and capable of handling the large numbers of samples that could be generated by air pollution control agencies and atmospheric research projects.

One could also add details like easy sample preparation, compatability with existing air collection methods, portability, low capital cost, ease of operation, etc.

Based upon work on light element detection by scattering accelerator beams for smog samples (first accomplished at Davis, although there is an alpha backscattering analysis of smog dating to 1950),[2] and the results of a Swedish group at Lund Institute of Technology which excited x-rays from a smog sample using an accelerator,[3] a proposal was submitted to Project Clean Air (PCA-038) which resulted in the following work statement.

Statement of Work

The Contractor shall within twelve (12) months from the date of
contract approval provide the necessary personnel, facilities, materials
and supplies to establish a charged particle--excited x-ray fluorescence
analysis system and to demonstrate and report on its capability for
determining the elemental composition of samples of airborne particulate
matter.

Specific tasks to be accomplished shall consist of the following:

(1) Design, construct and integrate into an operational system a
     charged particle beam, radiation shielding, beam collimator,
     sample holder, necessary detection and analytical equipment,
     and data recording equipment necessary to permit rapid
     analysis of airborne particulate matter samples.

(2) Perform enough measurements on standards to establish x-ray
     cross sections for elements of environmental interest.

(3) Experimentally evaluate the system design and establish its
     operational capability and sensitivity. This will be done by
     the analysis of a sufficient number of samples on a variety of
     commonly used filter media to insure the statistical validity
     of the results.

(4) Prepare and submit to the ARB technical monitor informal
     reports every three months. Prepare and submit a Formal Final
     Report fourteen (14) months after award of contract. The Final
     Report shall include: the details of the engineering design;
     systems operating procedures; sample collection and mounting
     procedures; report of the evaluation conducted under Task (3)
     above; analytical capability of the system including a matrix
     of detectable elements, associated sensitivity and standard
     deviation; and an estimate of equipment cost and operational
     cost on a per sample basis. The applicability of this type of
     analysis to other existing types of accelerators in California
     and throughout the United States shall be included in the report.

II. DESIGN OF THE UCD-ARB AEROSOL ANALYSIS SYSTEM

1. Choice of X-ray Detector

Since one of the above requirements was for detection of as wide a range of elements as possible at one time, an LN-cooled Si (Li) pulsed optical feedback system was chosen for the detector. This choice was based upon the use of K x-rays for elements from sodium through lanthanum, and the use of L x-rays for elements heavier than that. K x-rays were not used for heavier elements due to the rapidly falling cross sections for these elements and interference from soft gammas generated in the target.

Ge (Li) detectors remain a possibility for this work as their resolutions continue to improve, but at the time of purchase, the resolution of the Si (Li) detectors in in-beam conditions were superior. Extensive detector evaluations were held in winter, 1972, and three systems presented for evaluation proved adequate to the task.[4] However, none was able to properly correct for dead time (without being tuned-up on the sample in the beam) due to the necessity to observe low-Z x-rays, the noise generated by the accelerator, and the flood of light x-rays generated by bremsstrahlung in the target. The seriousness of this problem was not properly appreciated until late spring, 1972, and required extensive modifications of our operating systems. (See below)

2. Choice of Excitation

The choice of beam particle and energy for exciting x-rays in standard aerosol samples should be made upon some measure of the sensitivity achieved in the analysis. Since beam costs rise linearly with time, and the throughput of samples is inversely proportional to the amount of time spent on each sample, sensitivity per unit time was chosen as the criterion. Secondary effects such as target damage influence this judgment to some degree. A criterion was defined in terms of a minimally detectable peak, whose integrated counts were three times the error in the background under the peak, or

II. 2.1
$$N_x \geq 3\sqrt{N_B}$$

or
$$N_x / \sqrt{N_B} \geq 3$$

11

N_x = The number of x-rays in the peak.

N_B = The number of x-rays in the background under the peak, using average integration widths for the peak.

This definition conforms to standard definitions for statistical significance.

If we further define,

$$S_B = N_x / N_B$$

then this criterion reduces to:

II. 2.2 $\qquad \sqrt{N_x S_B} \geq 3 \qquad \text{or} \qquad N_x S_B \geq 9$

This criterion is used in the data reduction codes to reject peaks of dubious significance, despite the fact that peaks are often easily visible that do not satisfy this criterion. However, a very important consideration is that mistakes must be extremely unlikely, and, hence, a healthy conservatism must be a part of the whole system.

To investigate how this criterion governs the choice of excitation, one must know quite a bit about N_X and N_B. N_X is straight forward, depending on the cross section for producing an x-ray for an incident ion, or

II. 2.3 $\qquad N_x / N_i = \dfrac{N_o \rho t}{A} \left(\dfrac{d\sigma}{d\Omega} \right)_x d\Omega \, \delta \, \epsilon$

N_X = the number of x-rays seen in a detector

N_i = the number of incident exciting particles

N_o = Avagadro's number

ρt = the areal density in the sample of the element under study

A = the atomic weight of the element

$\left(d\sigma / d\Omega \right)$ = the cross section in cm^2/atom for emitting an x-ray into the detector at the angle θ for a specific incident particle and energy

$d\Omega$ = the solid angle of the detector in steradians

δ = dead time of the system

ϵ = detector efficiency

To insure highly accurate and quantitative results, elemental standards were used to determine the product $\frac{d\sigma}{d\Omega}\epsilon$. These foils were purchased from Micro Matter Corporation.[5] The foils used are listed in Table 1. The target thicknesses are also given. These are quoted to a precision of $\pm$ 5% by the manufacturer. A schematic of the system is given in Figure 1. An alpha beam from the cyclotron passes through a .6 cm diameter graphite collimator which is remotely readable and impinges on a thin target mounted at an angle of 45° to the incoming beam on a remotely controlled target wheel. The beam is then collected by the Faraday cup and integrated to a precision of about .2%. X-rays pass through a remotely controlled filter wheel, which was usually open for these runs, and a 25 micron Be window of a 10 mm^2 x 3 m LN cooled Si (Li) Detector and associated pulsed Optical Feedback circuitry. Data was accumulated in a PDP-15/40 computer with ND 2200 ADC's integral to the system. Beam currents were kept low to minimize dead time corrections and the results were verified with the beam pulsing system when it became available. Considerable care was taken to make certain that negligible amounts of beam were intercepted by the readable collimator directly in front of the target and to shield the Faraday cup. The detector resolution was approximately 170 ev during these runs.

The following equation was used for the calculation. (Equation II.2.3)

II. 2.4
$$\frac{d\sigma}{d\Omega}\epsilon = \frac{N_x}{N_i}\frac{A}{N_o \rho t}\frac{1}{\delta}$$

ρt = target thickness in gm/cm^2. The thicknesses of the targets were selected so that self-absorption correction would, for most foils, be only a few percent.

The total uncertainty in the product $\frac{d\sigma}{d\Omega}\epsilon$ is on the order of $\pm$ 7%.

Figure 2 shows total K emission cross sections for 30 MeV-α beams. The targets were also run at 16.5 MeV, 18 MeV, 25 MeV, 27.5 MeV, and some higher energies. In most cases the K_α and K_β peaks were individually summed to give a total K cross section. The K_α/K_β ratio is also thus obtained. Some typical ratios are given in Table 2. We shall see the importance of these ratios in the section on data reduction. Included
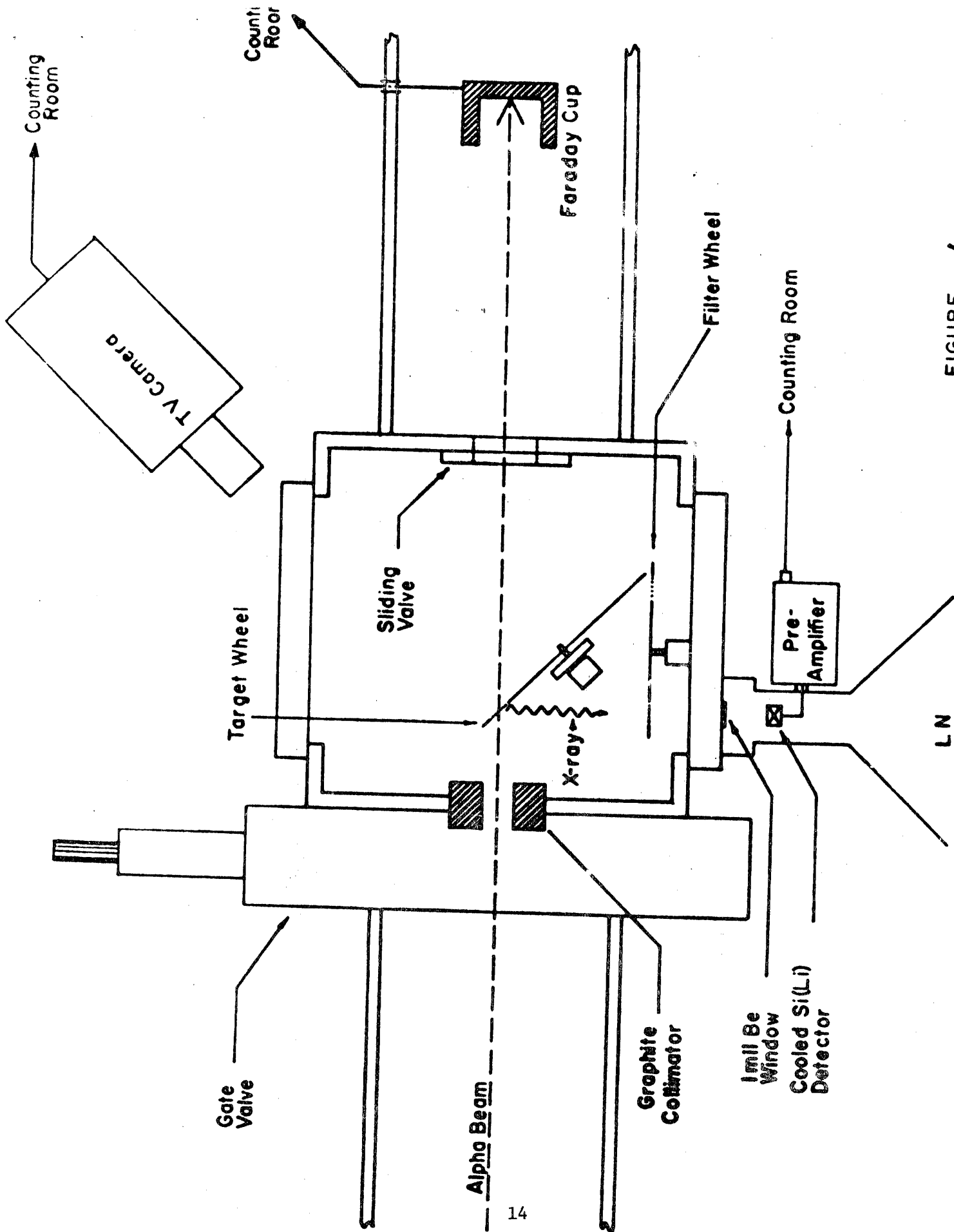
Counting Room

Counting Room

Faraday Cup

Filter Wheel

Counting Room

Pre-Amplifier

TV Camera

Sliding Valve

Target Wheel

X-ray

Gate Valve

Graphite Collimator

Imil Be Window

Cooled Si(Li) Detector

Alpha Beam

LN

14

FIGURE 1

30 MEV α's

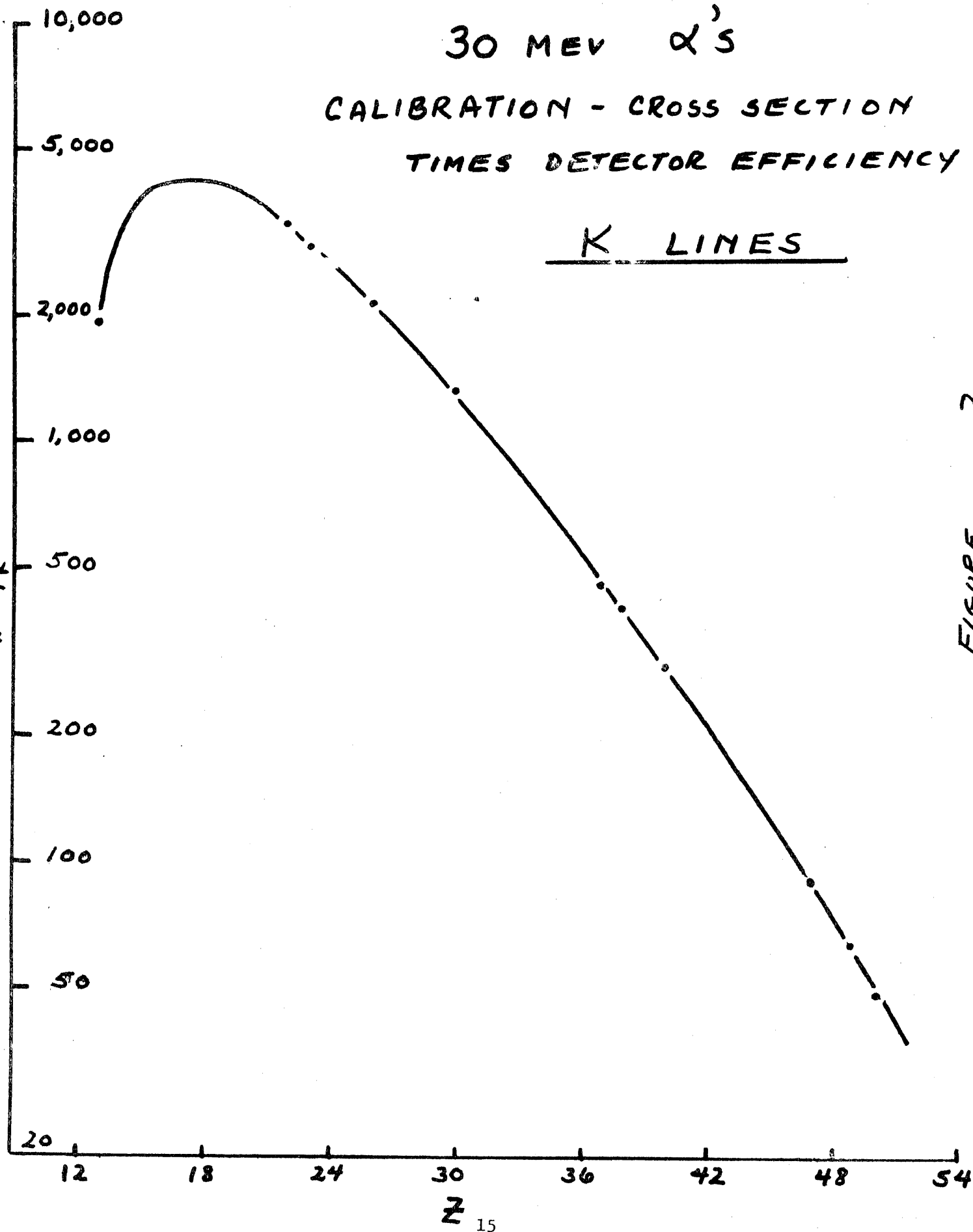CALIBRATION - CROSS SECTION

TIMES DETECTOR EFFICIENCY

K LINES

FIGURE 2

in Table 1 is a list of the characteristic x-ray lines that were obtained from each foil. As seen from the total K curve it is possible to interpolate between data points due to the smoothness of the curve.

Figure 3 shows a spectrum taken to obtain the L emission cross section for uranium.

Figure 4 shows the cross sections for total L emission. It must be pointed out that the term cross section here, as before, is used loosely. The term of course is the product of emission cross section and detector efficiency. Again, we were able to interpolate between data points for elements not run. Also given in Table 3 are typical L ratios.

The determination of N_B was more complex, in that it obviously depends on the nature of the substrate upon which the sample occurs. For this purpose, spectra were taken from various thin plastic foils (mylar, Kapton, teflon, polyethylene) of varying thicknesses as well as common filter substrates (Whatman 41, teflon nucleopore, Gelman GA-1, and Millipore EH, TFA, and several kinds of fiberglass blanks). The portion of the background under each possible characteristic x-ray peak was integrated, which gave N_B.

One fact was immediately evident. Fiberglass filters generally possessed such a variety of elements that it gave very poor sensitivity for most elements. Such substrates must be avoided if one wishes to use x-ray techniques, although some information can be gained if loadings are very heavy. In this situation, hwoever, absorption effects render the measurements usually non-quantitative. X-ray fluorescence seems preferable in such cases.

Limiting the discussion to substrates in which the heaviest element (in all but trace amounts), is fluorine or lighter, the background is a rather featureless continuum peaked at low x-ray energies, decreasing with increasing energy, and finally flattening at higher energies. See, for example, Figure 5, in which the shape of the background at 16.5 and 30 MeV can be seen.

This background can be explained as arising from two sources:

(1) Bremsstrahlung produced by electrons in the stubstrate scattered

TABLE 1

ELEMENTAL STANDARD	THICKNESS (TOTAL)	TRANSITION
NaCl	225 μgm/cm^2	Na K Cl K
Al	205 "	K
Si	162	K
CaF$_2$	248	Ca Kα,Kβ
Ti	181	Kα,Kβ
V	300	Kα,Kβ
Fe	325	Kα,Kβ
Ni	441	Kα,Kβ
Zn	535	Kα,Kβ
ZnS	257	S, K,Zn,Kα,Kβ
SrF$_2$	486	Sr Kα,Kβ
Zr	517	Kα,Kβ
Rh	265	Kα,Kβ
Ag	208	L ,Kα,Kβ
In	275	L ,Kα,Kβ
Sn	160	L ,Kα,Kβ
BaF	232	Ba,Lα,Lβ,Lγ,Ll
CeF$_3$	375	Ce,Lα,Lβ,Lγ,Ll
Sm	374	Lα,Lβ,Lγ,Ll
Tm	395	Lα,Lβ,Lγ,Ll
LuF$_3$	353	Lu,Lα,Lβ,Lγ,Ll
Ta	320	Lα,Lβ,Lγ,Ll
Au	354	M ,Lα,Lβ,Lγ,Ll
Pb	332	M ,Lα,Lβ,Lγ,Ll
Bi	450	M ,Lα,Lβ,Lγ,Ll
ThF$_4$	400	Th M ,Lα,L$\beta_{1,2}$,Lγ,Ll
UF$_4$	273	U M ,Lα,L$\beta_{1,2}$,Lγ,Ll

URANIUM L SUBSHELL X-RAYS

FIGURE 3

18

30 MEV α's

CALIBRATION - CROSS SECTION
TIMES DETECTOR EFFICIENCY

L LINES

TABLE 2

$K\alpha/K_\beta$ RATIO

	16.5 Mev α's	30.0 Mev α's
Ti	7.97	7.54
V	7.58	7.22
Fe	7.87	7.55
Ni	7.33	7.87
Zn	7.63	7 25
Rb	5.25	5.57
Sr	5.00	5.44
Zr	5.03	5.50
Ag	4.95	5.46
In	5.59	5.49
Sn	5.43	5.07

TABLE 3

$L\alpha/L_\beta$

	16.5 Mev α's	30. Mev α's
Ba	1.34	–
Ce	1.26	1.24
Sm	1.40	1.32
Ta	1.46	1.35
Au	1.76	1.52
Pb	1.83	1.47
Th	1.63	1.48
U	–	1.51

$L\alpha/L_\gamma$

Ba	9.05	–
Ce	9.15	8.09
Sm	11.11	8.99
Ta	10.86	8.25
Au	11.50	6.68
Pb	10.65	7.07
Th	10.21	7.63
U	–	7.46

$L\alpha/L\ell$

Ba	10.39	–
Ce	12.40	13.17
Sm	26.10	14.19
Ta	21.34	20.87
Au	20.73	19.58
Pb	18.07	18.13
Th	17.02	17.66
U	–	16.30

by the heavy incident particles. These electrons have a velocity that
can reach twice that of the incident particle, or

II. 2.5
$$E_e \leq \frac{4m_e}{M_i + m_e} E_i$$

where m_e is the mass of the electron and M_i is the mass of the
incident ion. This converts to an electron energy that, at its maximum,
can attain

II. 2.6
$$E_{e\,(max)}\,(kev) \simeq \frac{2}{M_i\,(amu)} E_i\,(Mev)$$

These electrons, stopping in the sample, produce a bremsstrahlung
continuum that, to first order, cuts off at

II. 2.7
$$E_x\,(kev) \simeq \frac{2\,E_i\,(Mav)}{M_i\,(amu)}$$

Note that a 16 MeV alpha particle and a 4 MeV proton both produce a
bremsstrahlung continuum cutting off at 8 KeV, since both particles have
the same velocity.

   (2) The second source of background arises from the soft gamma
tail due to compton scattering of energetic gamma rays. Since the
energy of gamma rays is generally for above the 30 KeV limit used for
the Si (Li) detector, this tail appears flat in the region above E_x (max)
from the bremsstrahlung.

   The shape of the background continuum is somewhat modified by self-
absorption of low energy x-rays by the foil and any loading present, by
more energetic x-rays from bremsstrahlung of heavier elements in a loaded
foil, by the escape of fast electrons knocked forward in very thin samples,
and effects associated with the detector itself.

   From these measurements, N_B was calculated, and the criterion was
applied to find the minimum detectable amount for each element. An
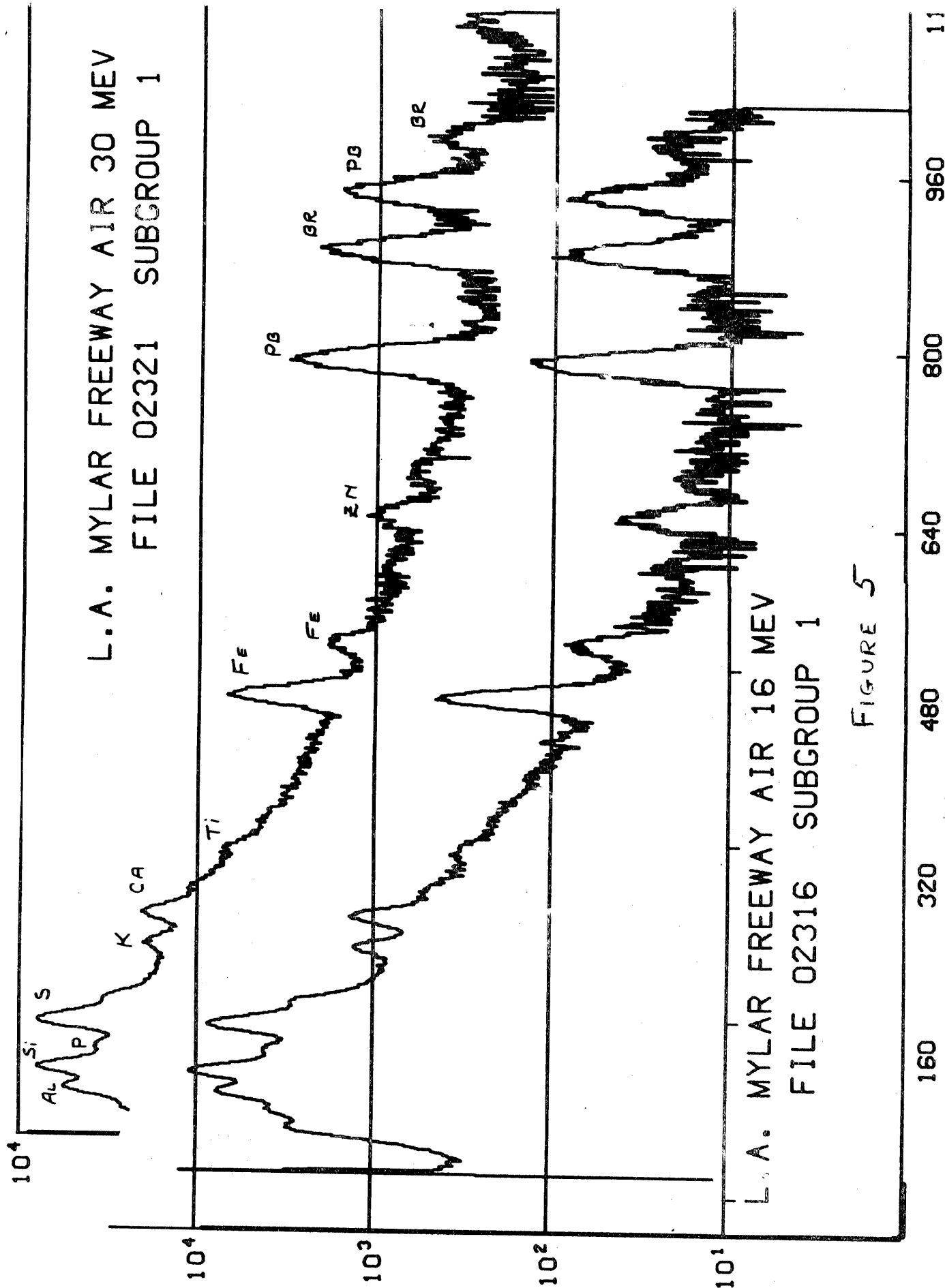approximate set of curves was drawn, and is shown in Figure 6 for 30 MeV.

22

L.A. MYLAR FREEWAY AIR 30 MEV
FILE 02321   SUBGROUP 1

L.A. MYLAR FREEWAY AIR 16 MEV
FILE 02316   SUBGROUP 1

FIGURE 5

23

DETECTABILITY vs. TARGET Z

10 μc of 30 MeV α's or 0.6 mg mylar

(APPROX.)

K LINES

L LINES
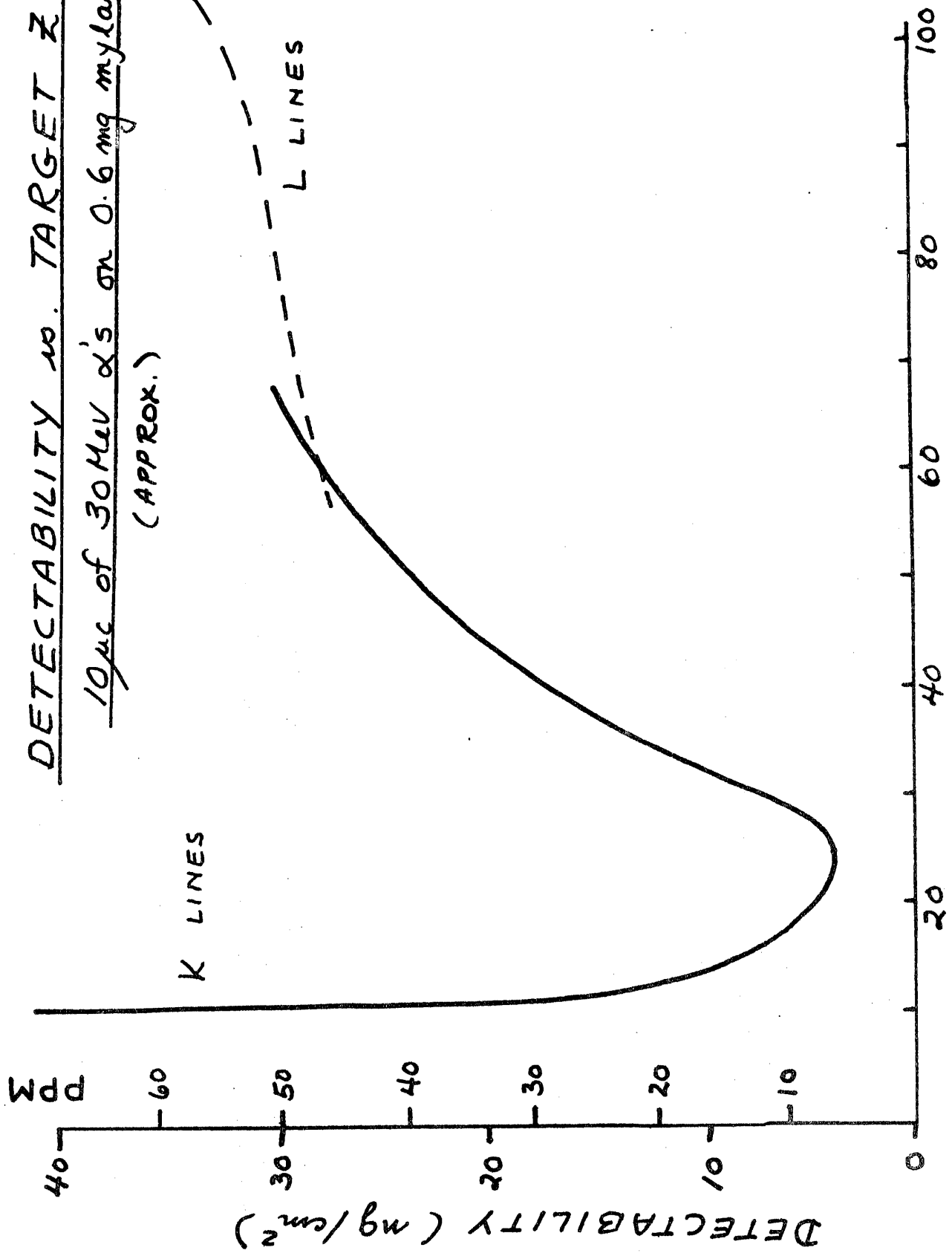
DETECTABILITY (mg/cm²)

Z

FIGURE 6

24

From measurements made between alpha energies 25 MeV and 80 MeV, it became evident that the optimum detectability occurred below 25 MeV for most elements, and, in fact, that an energy between 10 and 20 MeV was probably optimum. These beams were not routinely available at Crocker Nuclear Laboratory until summer, 1972, but these energies, as well as protons down to 4 MeV, can now be obtained at will.

Before these beams were obtained, a set of standard samples were sent around to several laboratories by Dr. John Cooper (Battelle Northwest), and the results showed that 4 MeV protons were superior to the 30 MeV alpha beams being used at this time.[6] Since, theoretically, 16 MeV alpha particles are about equivalent to 4 MeV protons, this encouraged us to lower the beam energy to these values. Runs were then performed to find N_x and N_B, confirming this prediction, and samples were run at both energies. One such comparison is shown in Figure 5. Sensitivity is gained in the region between potassium and strontium, as well as for heavy metals, and by the criterion used in this study, a factor of between one and three is gained by going from 30 to 16.5 MeV.

Would lower energies be better yet? Results at Brigham Young with 2 MeV protons indicated that any gain in signal to noise ratio S_B would be offset by decreased cross sections, so that detectability became worse.

An approximate summary of signal to noise ratios, obtained on a loaded Whatman 41 filter derived from data in the above study are given in Table 4.

TABLE 4

S_B

	Fe	Zn	Pb
30 MeV α	50:1	2.5:1	2.6:1
16 MeV α	60:1	9.5:1	6:1
4 MeV p	35:1	16:1	20:1
2 MeV p	20:1	2.5:1	2.5:1

Recall, however, that the criterion is $N_X S_B \geq 9$. For iron, N_X decreases by about a factor of 2 between 30 MeV α's and 16 MeV α's and at least a further factor of 2 between 16 MeV α's and 8 MeV α's (4 MeV p's to 2 MeV p's). A somewhat faster decline occurs for Zn and Pb.

Therefore, 4 MeV protons or 16 MeV alphas, corresponding to a velocity of about 3×10^7 m/sec., or about one-tenth the speed of light, seem to be optimal.

What about other particles, such as heavier ions or protons? Crocker Nuclear Lab can accelerate heavy ions such as ^{14}N that have the optimum velocity. However, our analysis indicates that not much is gained going to heavier particles. Once the velocity has been chosen at 3×10^7 m/sec., one gains sensitivity proportional to zinc, since

II. 2.8
$$N_X \propto Z_i^2 \quad \text{and} \quad N_B \propto Z_i^2$$

so that

II. 2.9
$$N_X / \sqrt{N_B} \propto Z_i$$

This appears in the result that one can use less beam current to get the same limit of detectability. A detailed comparison of protons and alpha particles of v= 0.1 c is given in Table 5.

This equality seems approximately satisfied when samples run at the University of Colorado are compared to similar runs at Davis.[7]

Since generally Crocker Nuclear Lab has beam currents far in excess of the requirements for this work, and since target damage may be the ultimate limitation to the technique, there are no present plans to use heavy ions at this time, although evaluations will be done to check these calculations.

3. Sample Handling

The requirement for being able to process large numbers of samples through the system with minimal hassle, and the optimum sample-detector geometry, led us to decide upon the use of 35 mm slides in

TABLE 5

Comparison of Proton and Alpha Beams (Approximate)

Assume: Each beam has 4 MeV/amu, and that one uses 10 µc of
protons and 5 µc of alphas. Values are r.lative to
proton values, Z_i being the incident charge and M_i
being the incid.. mass.

Factor	Protons	Alphas	Alphas numbers for 0.00015" mylar
1. X-ray Generation, $\dot{N}_x$	1	1	-
2. Background, N_b			
a) Bremsstrahlung	1	1	-
b) Compton	1	somewhat greater than 1	
3. Detectability	1	~ 1	-
4. Target Damage			
a) Energy loss rate (per particle)	1	$4\,(Z_i^2)$	200 KeV
b) Energy loss	1	1	20 mw at 0.1 µa
5. Multiple Scattering	1	$0.5\,(Z_i/M_i)$	0.3°
6. Kinematic Loss-Scattering	1	$4\,(M_i)$	-

Summary: 10 µc of 4 MeV protons is roughly equivalent to 5 µc of 16 MeV
alpha particles. The only major differences lie in multiple
scattering (less for alpha beams) and kinematical loss in elastic
scattering (greater for alpha beams, and hence, easier separation
of light elements). Similar reasoning applies to heavier ions for
integrated beam currents reduced by $1/Z_i$ to that for protons.

linear Bell and Howell or universal slide trays and a commercial slide changer to put the sample into the beam. The Bell and Howell mechanism was modified to work remotely, under computer control, while magazines were made to hold 108 samples at a time (3 trays).[8] Heat-sealable cardboard slides were used to mount the targets although plastic holders probably present smaller out-gassing vacuum loads.

Complete plans for the system are available upon request from Crocker Nuclear Lab.

4. Beam Geometry

The layout of the area is shown in Figures 7 and 8. A quadrupole doublet about 30 feet upstream of the system focuses the beam through slit S-1 to slit S-2. The magnification is such that it s impossible to focus all the beam through S-2, and, in fact, about 1/2 the beam is lost at that point. This produces a somewhat uniform beam image of about 0.2" width x 0.4" heighth on the target. The beam then passes through a Kapton isolation foil, designed to guarantee good vacuum at the Faraday cup. There follows five sample locations for further use of the beam. All are designed to use either the elastic scattering of alpha particles to detect light elements or an x-ray detector. Four are designed to hold standard slide frames, the fifth is a gas cell for gaseous samples. These samples cannot be changed remotely at this time. Finally, the beam enters the Faraday cup. It is then integrated by a Tomlinson current integrator, which provides the absolute calibration of the system.

Several options are available in this system. An isolation-diffusion foil (0.00015" Al) can be located at slit S-2, which results in more uniform beam intensity on the target, but a somewhat fuzzy edge to the pattern. A third slit, S-3, is being built to go directly before the target to clean up the edges of the pattern, provide alternative pattern sizes upon command, and allow normal use of the diffusion foil.

Finally, space is available for three additional fast target changers on this line. This would in principle quadruple the capacity of the system, if demand required it. However, beam pulsing (see below) would not be efficient in such situations, and thus, such an extension cannot
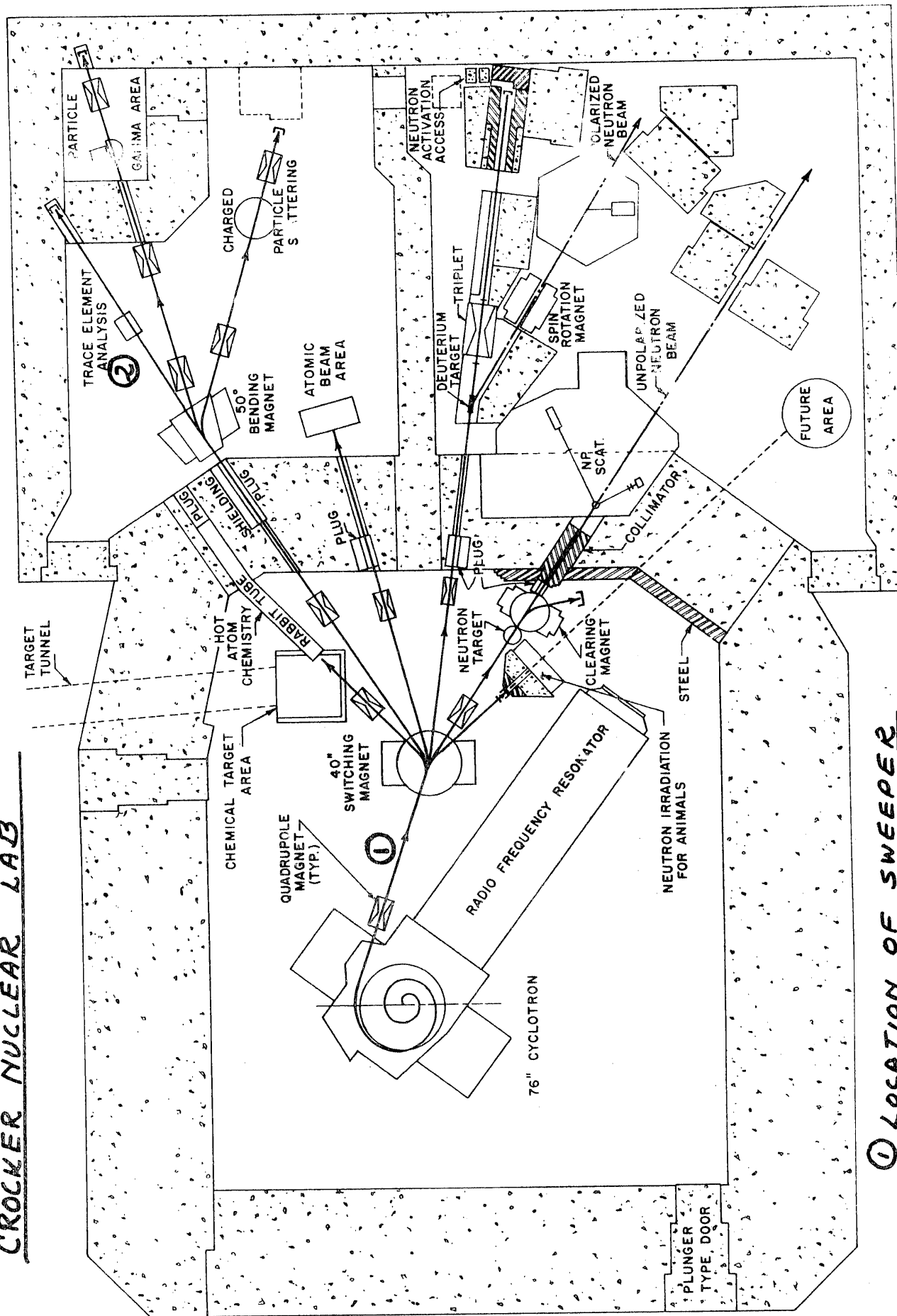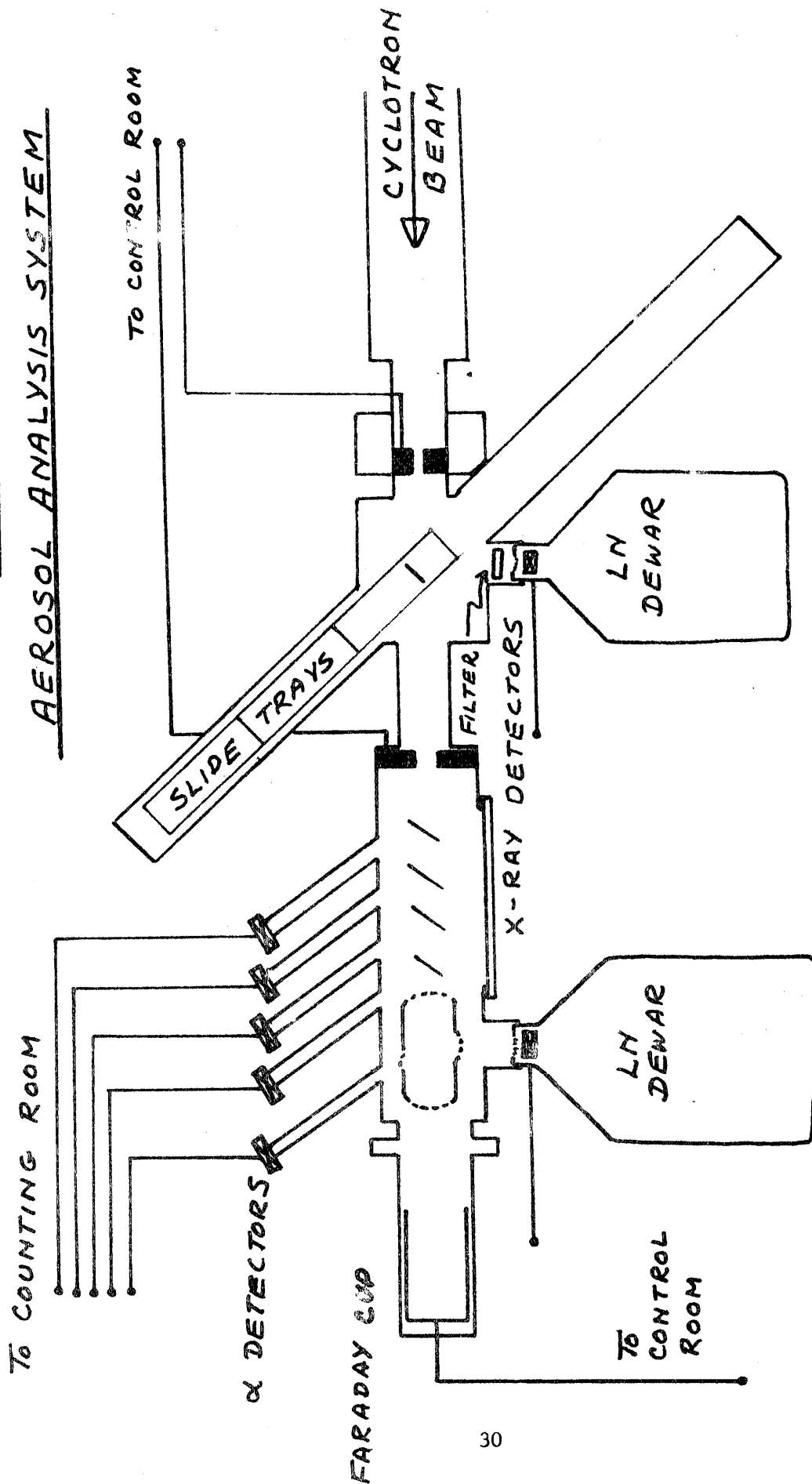
CROCKER NUCLEAR LAB

① LOCATION OF SWEEPER
② LOCATION - UCD-ARB SYSTEM

FIGURE 7

29

U.C.D.- A.R.B.

AEROSOL ANALYSIS SYSTEM

CYCLOTRON BEAM

To CONTROL ROOM

SLIDE TRAYS

FILTER

LN DEWAR

LN DEWAR

X-RAY DETECTORS

To COUNTING ROOM

α DETECTORS

FARADAY CUP

To CONTROL ROOM

30

be attempted until the dead time correction problem is resolved. If one
were not interested in elements around Na to Si, this expansion could
take place immediately. However, one of the advantages of accelerator-
induced x-rays is exactly in the detection of light elements, and such
modification is not planned for the present.

5. Decision to Use Beam Pulsing

The dead time correction problems alluded to in section (3)
proved very serious. The abundance of light x-rays in some samples (but
not others), combined with accelerator-associated electrical noise, resulted
in a target-dependent dead time correction. This is not the case for x-ray
excited systems, possibly because most of the x-rays in the spectrum come
from compton scattered exciting radiation, and cross sections for low
energy x-rays are small.

Two alternatives were possible:

(1) Reduce beam currents so that dead time errors were negligible,
or

(2) Place a source, such as 109 Cd, in each spectrum, and by
integration of the peak, evaluate the "true" dead time. The latter was
done as a stop-gap until a better method could be devised- that of
on-demand beam pulsing.

Beam pulsing as an answer to the dead time problem and as a way
to increase effective count rate, was suggested by the nuclear electronic
group at the Lawrence Berkeley Laboratory, the same group that originally
devised pulsed optical feedback. Dead time problems arise from the fact
that, while the detector-ADC system is processing a pulse, the system must
be protected from additional pulses piling up or the original pulse.
Since integration times are long in x-ray Si (Li) detectors, this dead
time becomes significant at relatively low count rates (few thousand counts
per second). The system protects itself against this eventuality through
use of a pulse pile-up rejector, which shuts down the electronics until
the system is ready to accept a new pulse. Since the accelerator beam
continues to generate x-rays from the sample during this period, the
results of the calculations based on the Faraday cup is also incorrect
unless it is correcte by a factor, δ. Systems to correct for this effect

have been successfully built, but for the reasons given above, they do not work well in the rather difficult conditions associated with an accelerator.*

In the alternative method suggested by the Lawrence Berkeley Lab group,[9] which they applied to x-ray tubes, the exciting source is turned off while the detector is dead. Thus, a monitor based on exciting current (such as a Faraday cup) reads correctly and the dead time is, in principle, zero. Other advantages accrue- especially higher effective count rates, and thus reduced data collection time.

The application of this idea to accelerators was suggested by the Lawrence Berkeley Lab group, and such a system was immediately built at Crocker Nuclear Lab.

The problems of on-demand beam pulsing at an accelerator are in some ways more difficult than for an x-ray tube. Pulsing the ion source is not useful, since too much time would elapse between a "beam-off" command from the detector and the time when the beam would indeed turn off. Therefore, it is necessary to pulse the full energy beam outside of the accelerator but in front of the x-ray system. This was accomplished at Crocker Nuclear Lab by designing and building a circuit to apply 4,000 volts to a pair of plates about one meter long. This voltage can be turned on at about 120 n seconds, left on for as long as is desired, and turned off in about the same time. Plans for the system are shown in Figure 9. The dead time with this system is shown in Figure 10. It can be seen up to 10,000 cps, the correction is (as predicted) negligible.

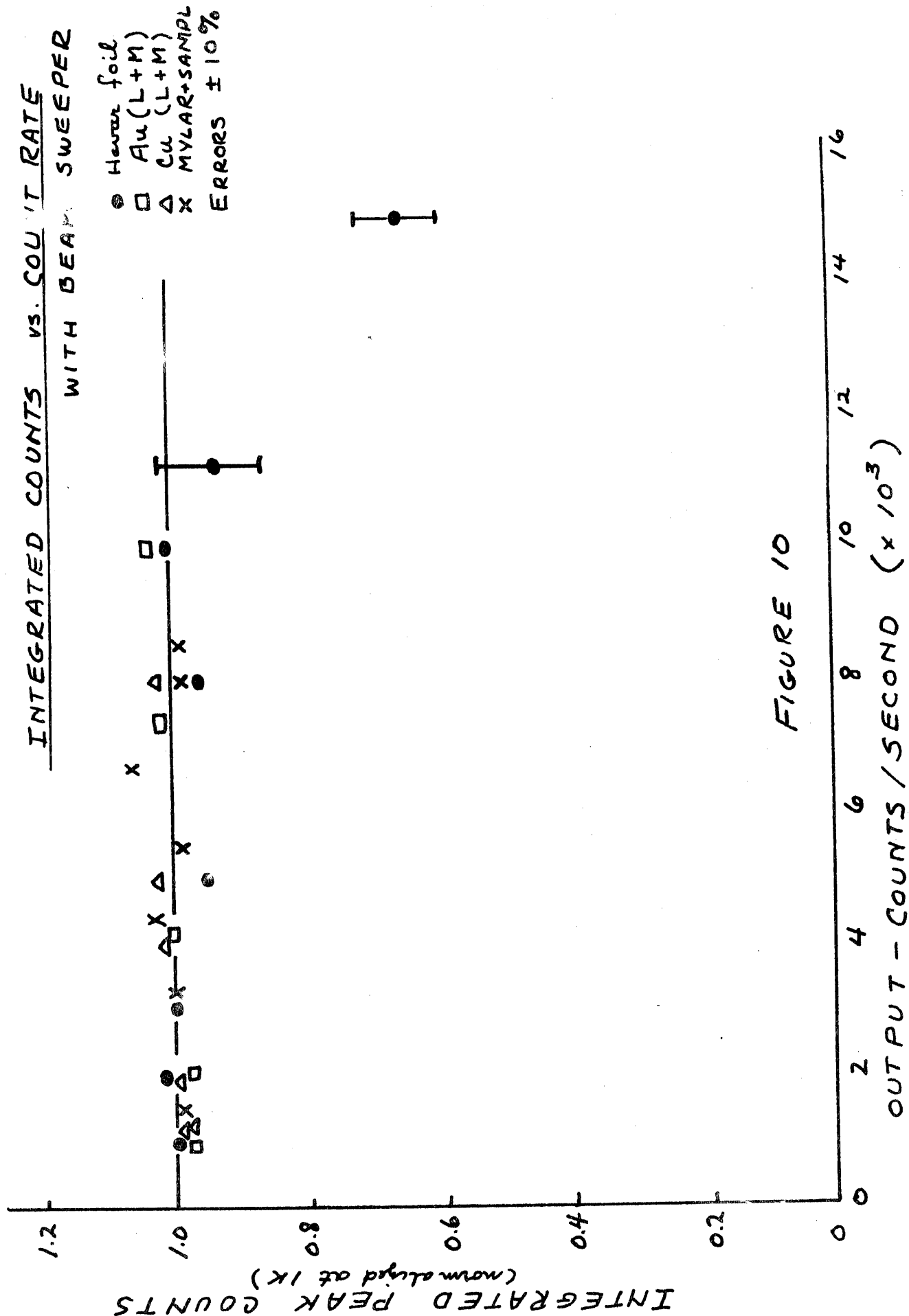Beam pulsing thus accomplished has a number of advantages:

(1) Dead time correction becomes very small and is sample-independent.

(2) Effective count rate in the computer at a given detector resolution increased since the input count rate almost equals the output count rate.

(3) Sample damage effects (see below) are reduced, since the beam is off when the detector is dead. This is more important for accelerators than for x-ray excited systems, in which sample damage is usually negligible.

* NOTE ADDED IN PROOF: Extensive modification of the electronics has resulted in good dead time correction for realistic samples at high count rates. Beam pulsing will continue to be used for the reasons given here.
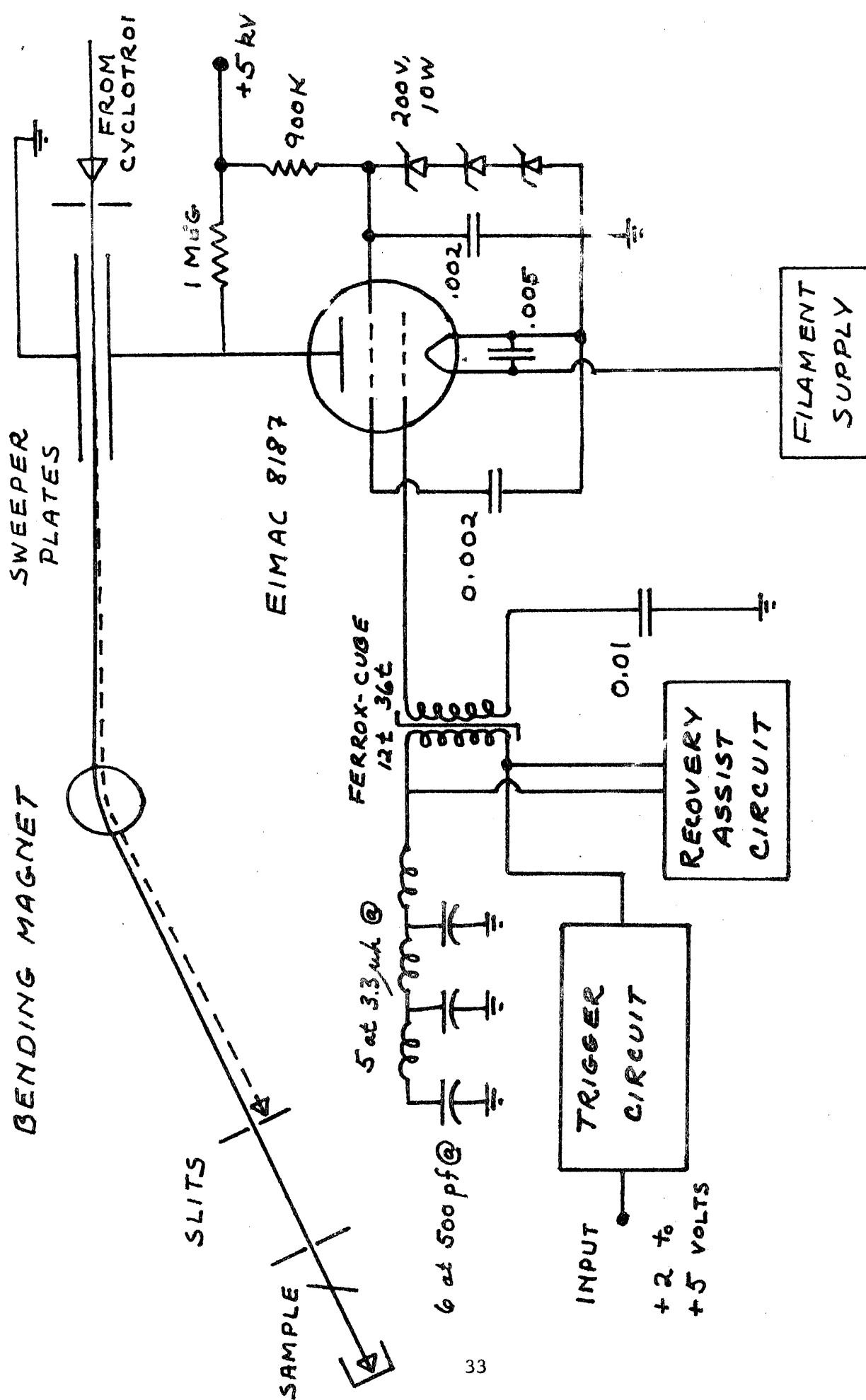
SCHEMATIC — DAVIS BEAM SWEEPER

FIGURE 9

33

INTEGRATED COUNTS vs. COUNT RATE

WITH BEAM SWEEPER

● Heavy foil
□ Au (L+M)
△ Cu (L+M)
✕ MYLAR+SAMPL

ERRORS ± 10%

OUTPUT - COUNTS / SECOND (× 10³)

FIGURE 10

INTEGRATED PEAK COUNTS
(normalized at 1K)

a multiplet (up to N = 4). If not, it is gaussian fitted as a singlet.

(9) From the gaussian fits, the true number of counts N_x is derived, and this value, with its error, is used in the reduction routine. The true energy, E_x, is also obtained at this time.

The operation of this code is shown in Figures 11 through 15 and Table 6. These integrations have been extensively checked against hand analysis, and the results agree within $\pm$ 15%.

Once one has obtained a true value for N_x, the number of counts located in the peak of energy E_x, there still can be an ambiguity in the element associated with the peak. The K_α transition of one element may fall close to the K_β transition of another, or an L transition may lie on top of a K transition.

The program prints out all possible interferences of this type, and calculates the amount of the element present under all the various assumptions. An example might be: (see Table 6)

$$E_x = 10.532 \text{ KeV} \quad \text{As (K}\alpha) \qquad 1874 \pm 562 \text{ ng/cm}^2$$
$$\text{or Pb (L}\alpha) \qquad 6354 \pm 1906 \text{ ng/cm}^2$$

The best way to discriminate between these choices is to use the redundancy inherent in fitting every peak. Therefore, one looks for the K_β line of Arsenic and the L_β line of lead. Thus, further down the analysis, one finds that:

(1) At location expected, for the K_β line of arsenic, no peak is found , thus setting a limit of 200 ng/cm^2 on arsenic present. (Obtained from the sensitivity curve generated during each run).

(2) At the location expected for the L_β line of lead, one finds

$$E = 12.606 \text{ KeV} \quad \text{Pb (L}_\beta) \qquad 5247 \pm 1574 \text{ ng/cm}^2$$

The combination of the absence of the arsenic K_β and the existence and amount of the lead L_β confirms the absence of arsenic above about a

TABLE 6

An example of the form of the output from the analysis program
as it existed in June, 1972.

X-RAY SPECTRUM ANALYSIS

SAMPLE - HID2 - 8
(6/72)

	CHANNEL	ENERGY (KEV)	COUNTS	ELEMENT	NANOGRAMS PER SQUARE CM	
PEAK NO. 1	53	1.432	10493.	AL	2981. +/-	894.
PEAK NO. 2	66	1.722	41064.	SI	7678. +/-	2303.
PEAK NO. 3	92	2.302	9282.	S	1493. +/-	448.
PEAK NO. 4	106	2.614	7107.	CL	1229. +/-	369.
PEAK NO. 5	137	3.306	7546.	K	1482. +/-	445.
PEAK NO. 6	154	3.685	9140.	SN	0. +/-	0.
				OR CA	1965. +/-	589.
PEAK NO. 7	190	4.488	1131.	SC	0. +/-	0.
				OR TI	384. +/-	115.
PEAK NO. 8	253	5.893	709.	MN	371. +/-	111.
				OR CR	0. +/-	0.
PEAK NO. 9	276	6.406	6843.	FE	4247. +/-	1274.
PEAK NO. 10	305	7.052	1208.	FE	5320. +/-	1596.
PEAK NO. 11	461	10.532	907.	AS	1874. +/-	562.
				OR PB	6354. +/-	1906.
PEAK NO. 12	522	11.892	1009.	BR	3020. +/-	906.
PEAK NO. 13	554	12.606	534.	PB	5247. +/-	1574.

← cross section not yet entered

← cross section not yet entered

38

X-ray Spectrum of Air Particulates from Fresno, Calif. (6/72)
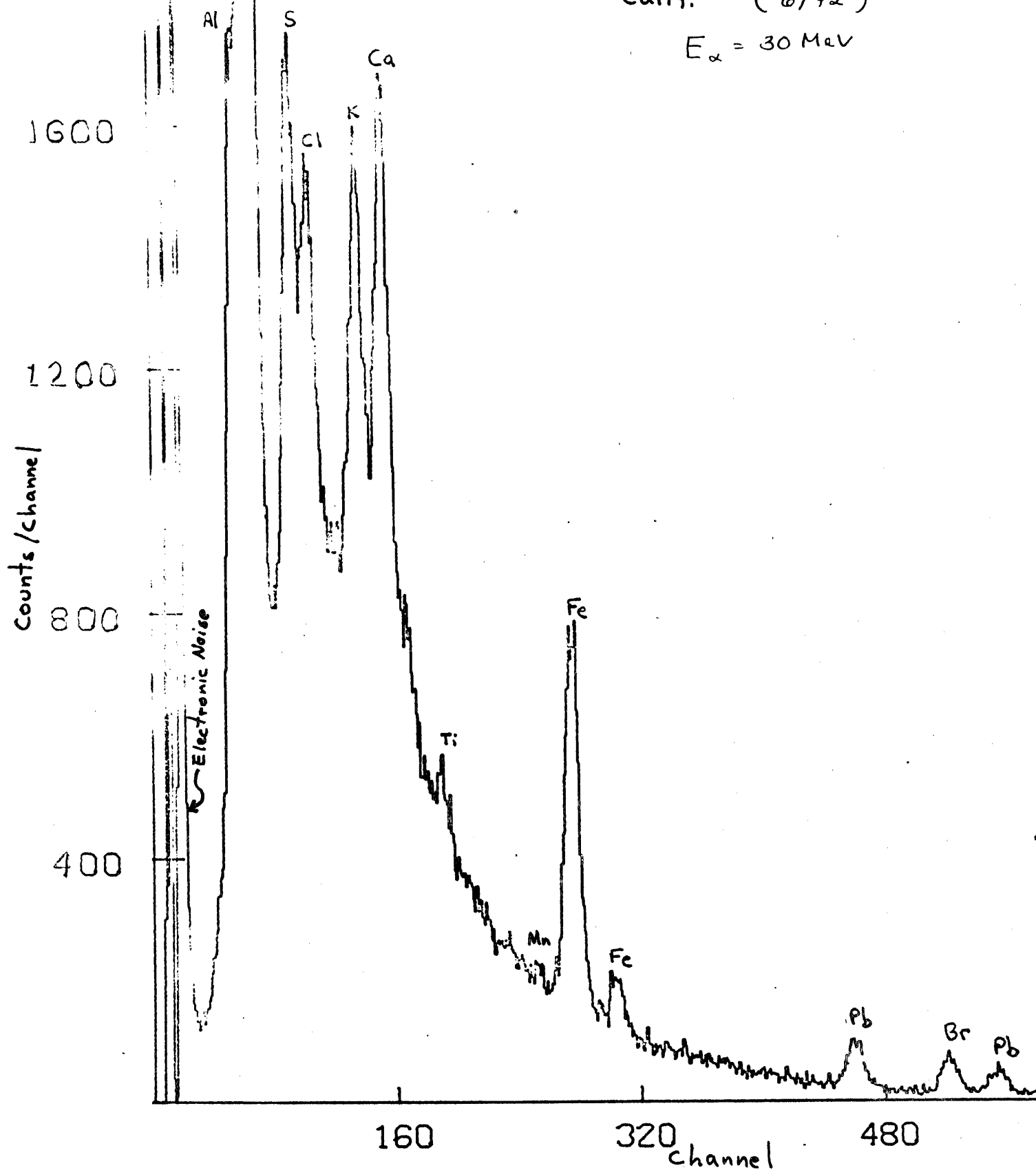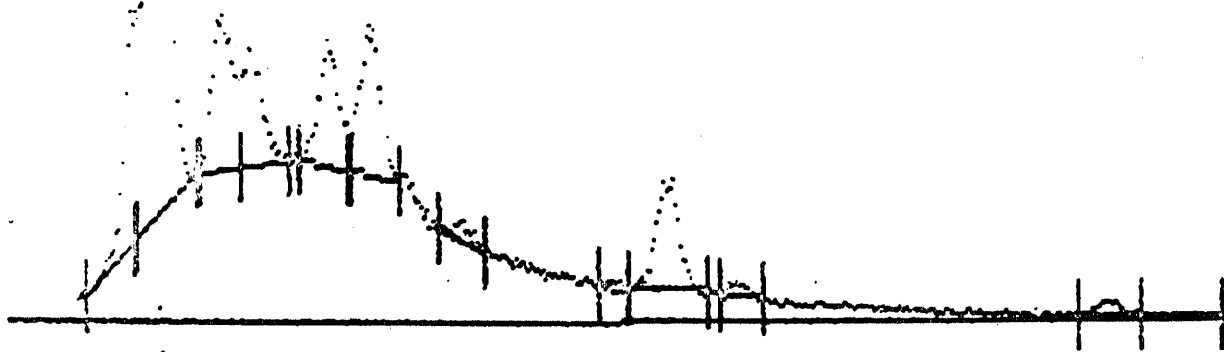
$E_\alpha = 30\ MeV$

39

FIGURE 12

INPUT TO COMPUTER

AVER. FWHM - 9

LIVE TIME - .7813

CHARGE - .5μ-coulombs

(6/72)

Orignial spectrum with cut-lines for integration of peaks

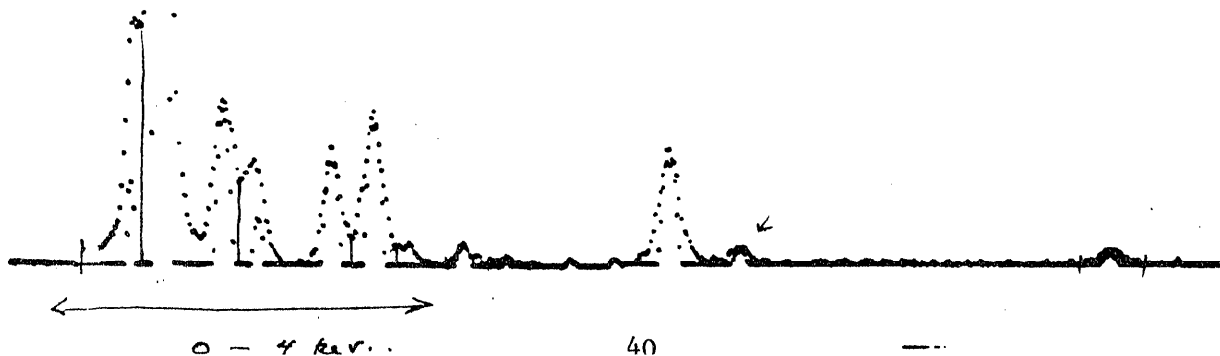Spectrum after Bremsstrahlung background has been removed; Corelation spectrum is seen under the data spectrum.

O — 4 keV.

40

FIGURE 13
Analysis Code as of 10/20/72
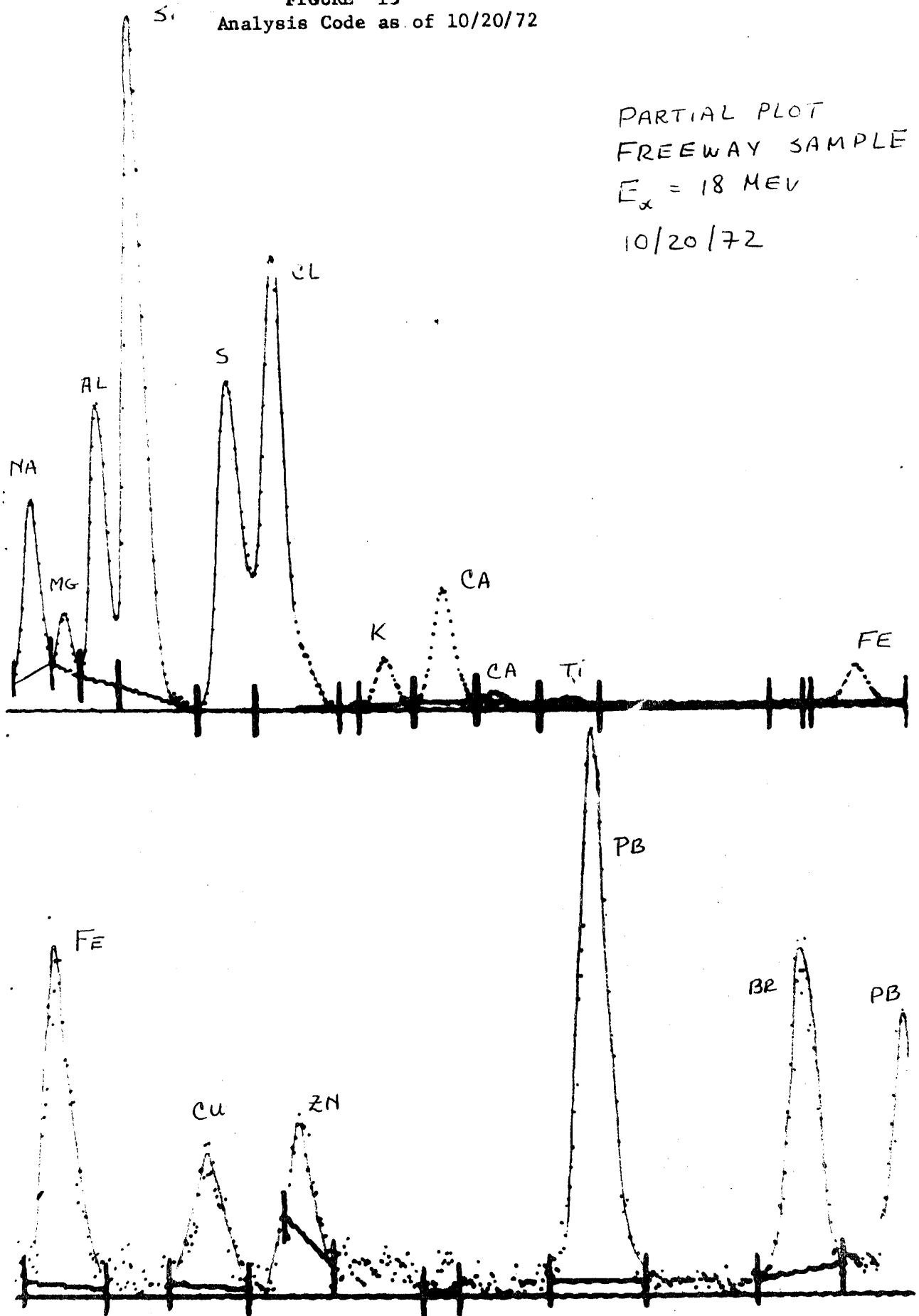
PARTIAL PLOT
FREEWAY SAMPLE
$E_x = 18$ MEV
10/20/72

FIGURE 14

A low-Z triplet, data and fit.

FIGURE 15

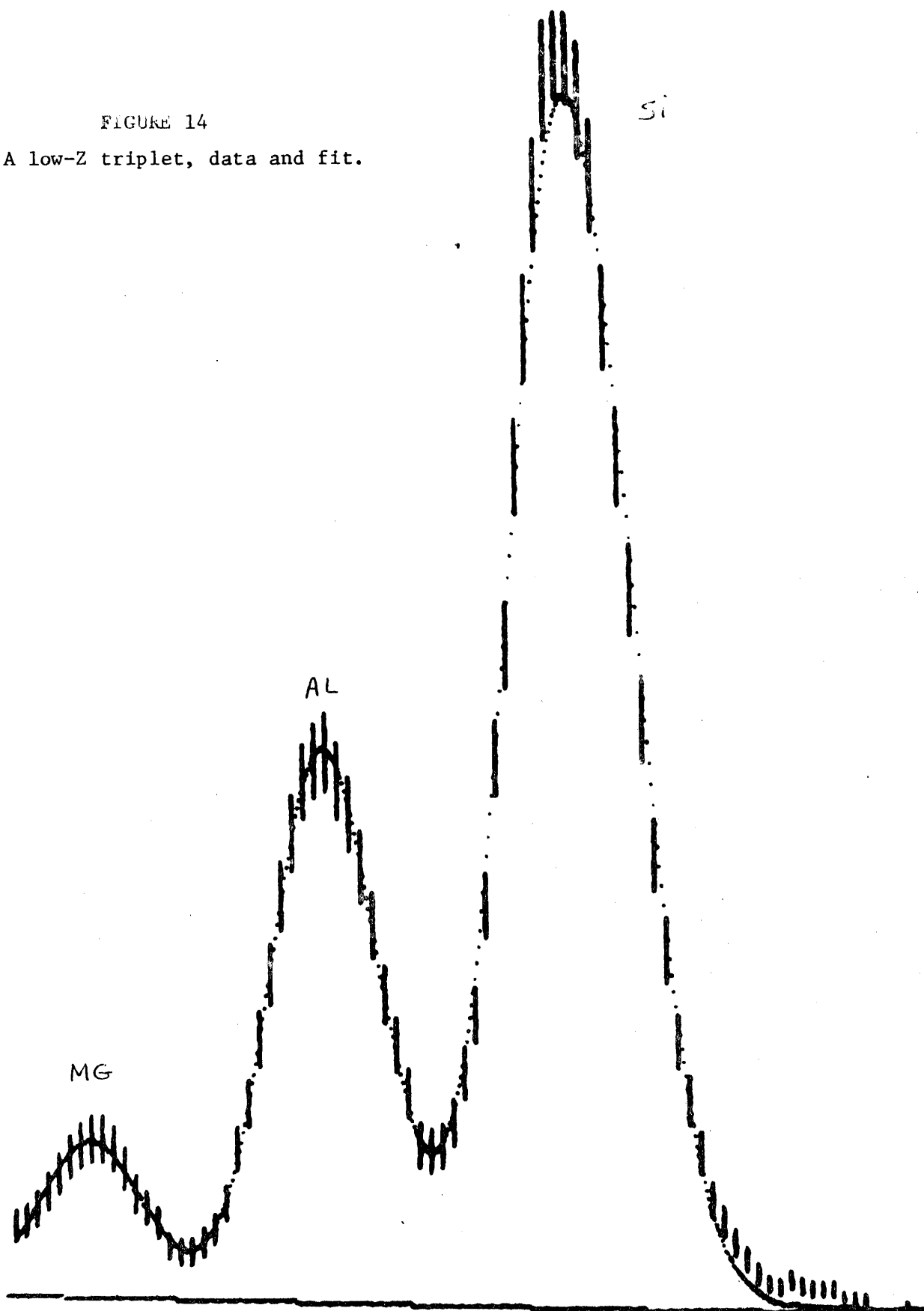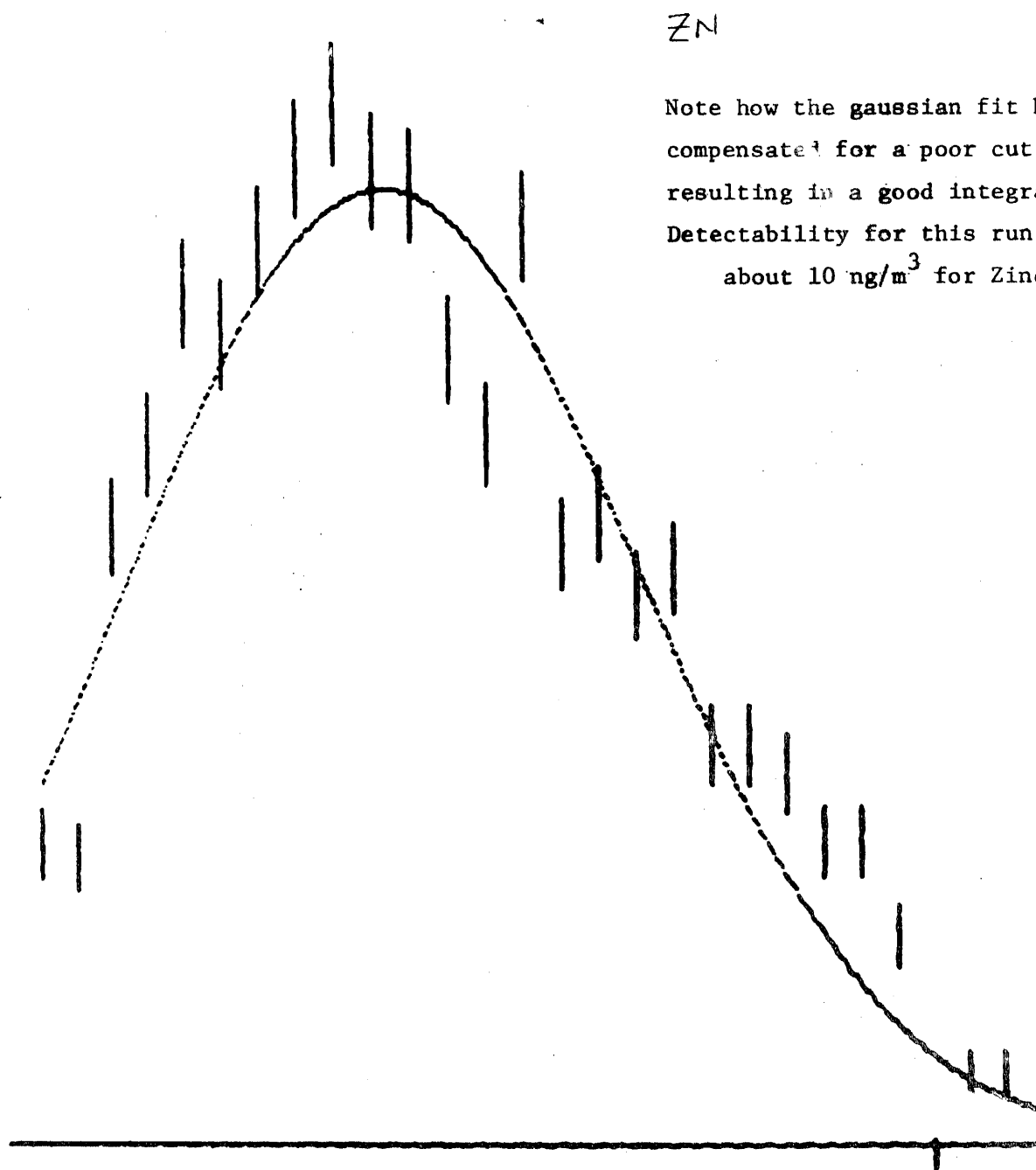Zinc peak in the same spectrum

ZN

Note how the **gaussian** fit has
compensate**d for a** poor cut point,
resulting in a **good** integration.
Detectability for this run –
about 10 ng/m^3 for Zinc.

200 ng/cm^2 value. If both arsenic and lead are present, one compares the difference in the lead values to the amount calculated using the K_β transition to set the amount of arsenic and lead present. Obviously, good resolution and a high degree of presicion in peak localization assets in reducing such interferences.

At this time, this calculation is still not left to the computer, since one must be certain that this operation is performed correctly. It is anticipated that this part of the code will be fully operational in a few weeks.

III. EVALUATION OF THE SYSTEM

1. Sensitivity

The sensitivity of the system can be expressed in terms of the minimum detectable amount of material that can be seen for a certain amount of excitation."

Once the choice of alpha particle energy has been made for the excitation, then the criterion

II. 1.1
$$N_x \, S_B \geq 9$$

could be applied element by element for certain assumptions regarding substrates. We used the alternative form of the expression, which seemed easier:

III. 1.2
$$N_x / \sqrt{N_B} \geq 3$$

By measuring the value of the background at the location corresponding to E_x, and using the normal integration widths for a peak, it was possible to generate the integral of the background, N_B, for a given substrate. Such a detectability curve for 30 MeV alphas on 0.00015" mylar is shown in Figure 6.

It can be seen that this curve is stated in terms of a given integrated beam charge in microcoulombs. The sensitivity then scales in proportion to the square root of the charge. Note that this result is

equivalent to only a moderately good measurement in terms of parts per million.

The implicit assumptions in this graph are that one has an interference free measurement, that loadings are so light that self absorption is small, and that one has the exact geometry presently used in the system. Since there are plans to increase the solid angle of the detector, these results will change as far as the amount of charge necessary to obtain a given sensitivity is concerned.

Note that no information is given on how long it takes to accumulate the integrated beam charge shown above. If the sample is very lightly loaded and is layered on clean 0.00015" mylar, then one can use beam currents of 300 nA or more, resulting in 10 μc of beam in about 30 seconds. The limitation is set by the count rate of the detector, since it is always possible to obtain good count rates for these samples no matter how lightly loaded. If, on the other hand, the sample has lots of iron or lead on it, the count rate may exceed present limits, and the beam current will have to be lowered, sometimes to as low as 0.3 nA or less for heavily loaded fiberglass samples. Obviously, the same charge could be accumulated in this latter case, but it would take a longer time. Therefore, the system tends to run in a variable sensitivity mode, where the sensitivity is the best for lightly loaded samples and poorer for heavily loaded samples. This suits this type of analysis, which is elemental as opposed to trace elemental. For, if one runs a heavily loaded sample to high sensitivity, one tends to be bothered by background generated by the big peaks, spurious effects such as small single escape peaks and pile up peaks, and other effects that confuse the analysis.

Often, sensitivity can be gained for medium and heavy elements by interposing a low-Z (CH_2) filter (32 mils) between the sample and the detector. This cuts out the abundant low-Z elements and allows one to run higher beam currents for a given count rate in the detector. This technique is especially useful for non-smog samples. Sample calculations of sensitivity for some common substrates are shown in Table 7, and two typical analyses, one for 0.00015" mylar and one for Whatman 41, are shown in Figures 16 and 17.
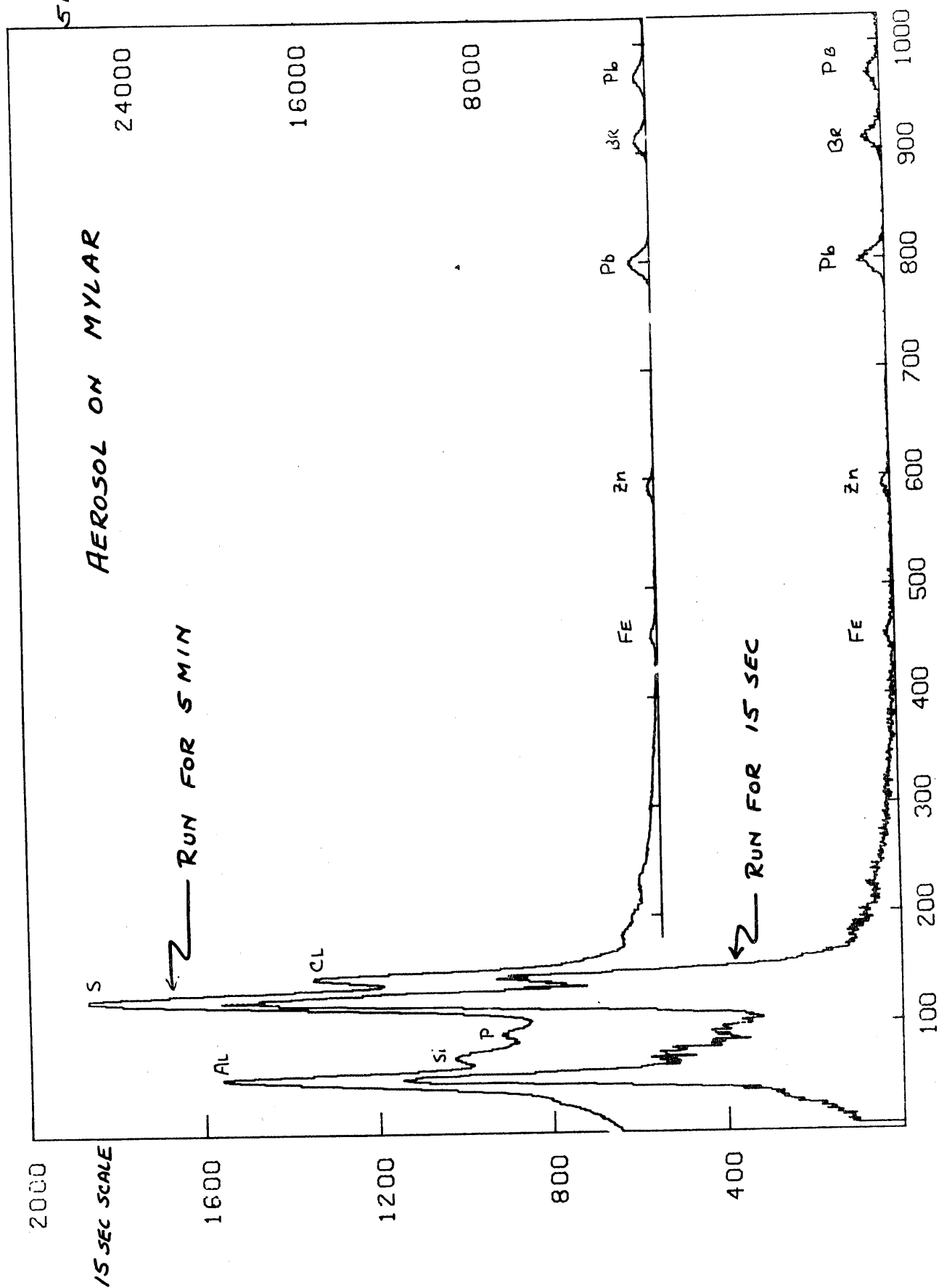
AEROSOL ON MYLAR

FIGURE 16

46
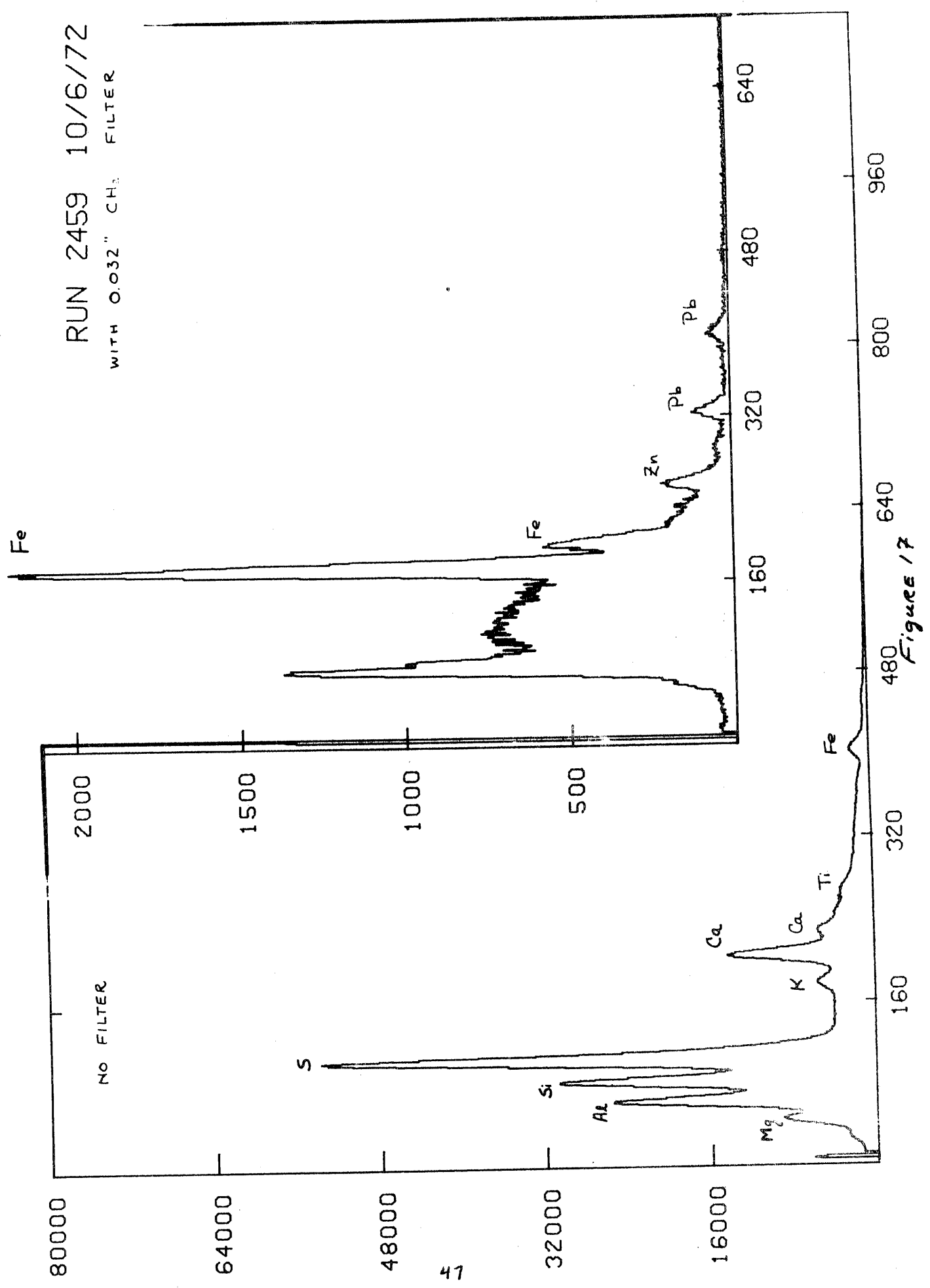
RUN 2459 10/6/72

WITH 0.032" CH₂ FILTER

NO FILTER

Figure 17

TABLE 7

Limits of Detectability for
Aerosol Samples Collected by Several Commonly Used Techniques

ASSUME: 10 c of 30 MeV alpha particles

1. For a 0.00015" mylar (or other similar plastic) substrate, the average limit of detectability is about $20ng/cm^2$ (Figure 6).

   (a) The sampling d. .ce is a Lundgren impactor, operating at 4 cfm and a 24 hour rotation rate.

   Area of substrate is about 63 cm^2 for 24 hours.
   Integrated air flow is about 192 m^3.

   $f = 63\ cm^2/192\ m^3 = 0.33\ cm^2/m^3$

   Limit of Detectability, D, = $(20\ ng/cm^2)(0.33\ cm^2/m^3)$

   or, $\boxed{D = 7\ ng/m^3}$

2. For a Whatman 41 filter (or other similar material) of thickness 8.8 mg/cm^2, the average limit of detectability is about 70 ng/cm^2.

   (a) The sampling device is a Hi-Vol run for 24 hours at 40 cfm.

   Area of substrate is about 400 cm^2.

   Integrated air flow is about 1920 m^3.

   $f = 400\ cm^2/1920\ m^3 = 0.21\ cm^2/m^3$

   $D = (70\ ng/cm^2)(0.21\ cm^2/m^3)$ $\boxed{D = 15\ ng/m^3}$

   (b) The sampling device is a "Lo-Vol" operated at 2 cfm and using a 47 mm diameter filter.

   Area of substrate is about 16 cm^2.

   Integrated air flow is about 96 m^3.

   $f = 16\ cm^2/96\ m^3 = 0.16\ cm^2/m^3$

   $D = (70\ ng/cm^2)(0.16\ cm^2/m^3)$ $\boxed{D = 11\ ng/m^3}$

   (c) The sampling device is a C.O.H.-type device that pulls 1000 litres through a 1.2" diameter filter.

   Area of substrate is about 6 cm^2.

   Integrated air flow is about 1 m^3.

   $f = 6\ cm^2/1\ m^3 = 6\ cm^2/m^3$

   $D = (70\ ng/cm^2)(6\ cm^2/m^3)$ $\boxed{D = 420\ ng/m^3}$

   (d) The sampling device is a portable aerosol monitor that runs at 0.1 litres/sec for 8 hrs with a 1 cm^2 filter.

   Area of substrate is 1 cm^2.

   Integrated air flow is about 0.024 m^3.

   $f = 1\ cm^2/0.024\ m^3 = 40\ cm^2/m^3$

   $D = (70\ ng/cm^2)(40\ cm^2/m^3)$ $\boxed{D = 2.8\ \mu g/m^3}$

48

2. Error Analysis

The following table indicates the sources of error present and their probable value for routine analysis. Referring to our formula, (II. 2.3)

III. 2.1

A	atomic weight	no error
N_i	integration of beam	$\pm$ 1%
N_o	Avogadro's number	no error
δ	dead time correction	< 5%
$\left(\dfrac{d\sigma}{d\Omega}\right)_{\epsilon x}$	measured from standards	$\pm$ 7%
$d\Omega$	solid angle	$\pm$ 1%
N_x	statistical error	$\pm N_x$
	+ fitting error	variable, 5-20%

3. Matrix Effects

The most serious correction, and thus, the largest possible source of error, depends upon the self-absorption of light x-rays due to the loading of the sample or due to a certain filter media. These errors have been estimated by using a model for the composition of an urban aerosol, consisting of 60% light elements (H, C, N, O) and the remainder distributed among Si, S, Ca, Fe, Br and Pb roughly according to values seen in Los Angeles smog. If we assume a loading of 120 $\mu g/m^3$ in an urban atmosphere, with about 1/3 of this appearing on any given drum of a Lundgren impactor run at normal operating conditions (24-hr. rotation and 4 cfm), a loading of about 100 $\mu g/cm^2$ will result on a drum. These results are shown in Table 8.

If we likewise assume that under the same atmospheric conditions, a Hi-Vol is run for 24 hours with a Whatman 41 filter (400 cm^2 and 2000m^3), loadings of about 500 $\mu g/cm^2$ will result. Assume that 2/3 of the material resides in the front half of the filter and 1/3 in the back half of the

filter, the following self absorption is calculated:

TABLE 8

Self Absorption of a Standard Aerosol on Mylar & Whatman

	Mylar	Whatman 41			Mylar	Whatman 41
Na	14%	98.3%		S	3%	70%
Mg	10%	95.5%		Ca	1.3%	35%
Si	5%	87 %		Fe	<0.5%	9.2%
P	4%	80 %		Pb	<0.5%	2.5%

Experiments are now in progress to determine the accuracy of these calculations. One such experiment involved Whatman 41 filters analyzed by atomic absorption for K, Ca, Fe, Cu, Zn, and Pb.[*] Comparisons with the UCD-ARB system for absolute amounts were within experimental error for all these elements. Other comparisons against neutron activation analysis and x-ray fluorescence are continuing, but early data indicates generally satisfactory agreement at least down to potassium on Whatman 41. However, as seen in the table, for the loadings normally encountered, these effects are generally not very significant for mylar foils and membrane-type filters, but are quite significant for low-Z elements deposited on a Whatman 41 filter.

4. Beam Damage

The ultimate limitation for elemental analysis by ion-induced x-ray emission is probably set by target damage, since abundant excitation is available for almost any sample. To clarify various aspects of this problem, we can identify various levels of damage.

Level I.   No changes in target composition other than those associated with the delay between sample collection and analysis, assuming careful handling and no contamination.

* courtesy of Dr. Donald Gatz, Illinois State Water Survey, Urbana, Illinois.

50

Level II.   Changes occur which, although they do not
                   modify the results of this analysis, inter-
                   fere with future analyses of the same sample.

Level III.   Changes occur which result in errors in the
                   present analysis. Varying levels of error
                   are introduced from barel, perceptible to
                   extreme.

First, there can be losses induced by the fact that the samples are present in a vacuum. Studies have been done on vacuum induced losses using x-ray fluorescence at Davis. The samples were smog samples from the Bay Area, and were analyzed in air for elements between Ca and Pb. Elements seen were Ca, Fe, Zn, Br, Pb. The samples were then subjected to vacuum for lengths of time varying from 30 minutes to 2 hours. To within the limit of accuracy, $\pm$ 20%, no loss was observed in any of these elements.

To study the effects of beam damage, several foils were respectively analyzed to see if decreases were seen in the elements. The results of one such series is given in Table 9. This was performed on a mylar base of 0.6 mg/cm^2, and the integrated flux was about 60 times that normally used. Possible loss is observed for Si and Br, but it is not statistically certain.

Results using the substrates mylar, Kapton and teflon, were all similar, in that some darkening could be observed of the plastic for integrated fluxes above 20 µc. Nevertheless, there was no indication of target substrate failure of major losses of elements.

Finally, about 20 Gelman GA 1 filters were analyzed in the beam. These filters showed two types of damage, both severe:

(1) A darkening and embrittelment of the center occurred for integrated fluxes above about 5 µc. The filter often split or cracked after several days, and was generally hard to handle.

(2) Two filters simply exploded after being subjected to a flux between 1 µc and 10 µc. Rather neat rectangular holes were created in the substrate, and the pieces did not appear to be charred. One possible explanation was that these filters had absorbed some water. The poor conductivity of Gelman GA 1 then allowed the water to become steam,

51

TABLE 9

Examination of Possible Elemental Loss
During Bombardment-Long Term Effects

Atmospheric Aerosols on Mylar-(580 $\mu g/cm^2$ or 0.15 mil)

I_{ave} = 50 nA; P_{ave} = 10 mw; Normal Charge – 10 μc

(Normalized to amount in box; all measurements absolute)

Charge (integ.)	Si	S	K	Fe	Br	Pb	Br/Pb	Ave.(all)
20 μc	1.00	1.00	1.00	–	–	0.93	–	0.98
40 μc	0.92	0.91	–	–	–	–	–	–
140 μc	1.00	1.12	0.81	1.00	1.00	1.00	.25	0.99
240 μc	1.05	1.17	1.04	0.87	0.90	1.11	.20	1.03
340 μc	1.96	1.47	1.15	0.91	1.19	1.35	.22	1.18
540 μc	0.79	1.21	0.92	1.02	0.84	1.19	.17	1.00

Errors ± 15%

fracturing the stubstrate. For whatever the reason, this substrate does not seem suited to this type of analysis. Reasons for these results are under study.

A heavily loaded Whatman 41 filter was subjected to 30 μc of 30 MeV alpha beams, and 35 minutes later, checked with a GM ounter for induced activity. Approximately 1.5 mr/hr was recorded on contact. Since most analyses take place at 16 MeV (where the effect is ~1/4 that at 30 MeV) and for loadings and beam fluxes lower than the above values, the effect does not seem serious. Incidentally, decay was rapid, and after a few hours, no detectable activity was recorded.

Heavily loaded Whatman 41 filters were run to destruction (about 50 μc in 10 minutes) whereby the center darkened and split. The cracking of the foil generally resulted in a reduction of the calculated amount of material present, since the beam would pass through the holes without exciting the x-rays. Even in these extreme conditions, no evidence for consistent or preferential loss of certain elements was observed. Much more data must be gained, however, before such conclusions can be stated as certain. In practice, beam currents and integrated fluxes are being held well below such levels of damage, and the mitigating procedures mentioned below should reduce the problem by a factor of about 20.

What can be done to reduce these effects?

(1) Use as large a detector area as possible, thus increasing the number of x-rays per unit beam flux. However, resolution may suffer if the area becomes too large. Plans are to go from 10 mm^2 to 30 mm^2 when funds permit.

(2) Move the detector as close to the sample as practicable.

(3) Use as large an area of irradiation as possible. A beam area of 0.4 cm^2 was used for these studies, due to special requirements of one of the users, but normally an area of about 1.5 cm^2 will be used. This reduces these effects (except for activation) by a factor of about 4. Eventually, sample size becomes unwieldy and beam uniformity suffers if the irradiated area becomes too large.

(4) Use thin substrates whenever possible. In cases where ultimate sensitivity is required ($\sim 10^{-12}$ gms), thin carbon foils can be used, which generally are not damaged by accelerator beams. However, putting

a sample on thin carbon films is often difficult or impossible, thus this approach has limited value.

(5) Use of beam pulsing has already reduced beam damage below the levels reported above. Assume the dead time for a measurement which results in N_x x-rays in the computer is δ, and the charge necessary to generate these x-rays is Q. Then, with beam pulsing, the charge necessary to generate the same number of x-rays N_x is the computer, Q_p is related to the previous amount of charge, Q, by-

$$Q_p = Q \, (1 - \delta)$$

Since, before pulsing, dead time was generally significant for all samples, and since abundant excitation is available for any sample no matter how lightly loaded, the reduction in target damage has been almost a factor of 2.

(6) Samples that are suspected to have such problems can be specially prepared by spraying the surface with clear plastic Krylon spray (#1301), which virtually eliminates vacuum effects and reduces loss of volatiles due to beam heating. In extreme cases, the sample can be layered with mylar, which provides almost total containment of volatiles but does not prevent changes in the sample due to heating.

In summary, the use of beam pulsing and a normal 1.5 cm^2 irradiation area has reduced damage effects by a factor of about 8 over the results of the early studies reported here. These, plus the use of a 30 mm^2 detector, will then give a net reduction of about a factor of 24 in beam effects, and such effects shall be unimportant in most cases.

5. Very Light Elements by Alpha Scattering

The detection of light elements by alpha scattering has been used for decades, and, in fact, there is a measurement of elements in smog dating to 1950. However, most of these measurements used alpha-emitting sources and backscatter from a thick target. In summer, 1970, the group at UCD performed measurements on thin gas and solid targets using forward scattered alpha particles from a cyclotron and modern solid state detectors. The sensitivity proved surprisingly good, and this type of analysis is used in the five target stations behind the fast target changer.

The theory behind the method is elementary. If a particle scatters from another particle, energy is lost to the kinematic recoil of the struck particle. The energy loss, ΔE, is (non relativisitcally)-

III. 5.1
$$\Delta E = \frac{2 M_1 M_2}{(M_1 + M_2)^2} \left(1 - \cos \phi_{cm} \right) E_i$$

M_1 = incident particle mass

M_2 = target particle mass

ϕ_{cm} = center of mass angle of the scattered particle

E_i = incident particle energy

The same formulas hold for the calculation of ρt as were used for x-rays, but the mechanism and the values are quite different (Formula II. 2.3). In particular, the probability of a scattering event is reduced by the fact that nuclear cross sections are involved rather than atomic cross sections, which gives a probability for an event reduced by a factor of about 1,000. Thus, sensitivities are in $\mu g/cm^2$ rather than ng/cm^2. This loss can be somewhat mitigated by the fact that loadings of material in the sample can be much higher than what is normal for x-ray analysis of light elements, so that a net factor of about 100 remains. Since so much more integrated flux is required to obtain adequate sensitivity, five sample locations were included behind the fast sample changer. Samples located there are changed only when a full load of 100 slides are changed. The beam that passes through the slides thus is utilized several times before entering the Faraday cup.

One factor must be carefully evaluated, however. If the beam is multiply scattered so that it misses the Faraday cup, the absolute values for the data on the fast changer will be too high. These losses have been investigated, and for thin plastic substrates, and 0.5 mil Be secondary foils for the alpha scattering, the effect is < 2%.

The most unfortunate aspect of this method lies in the fact that, if one wishes to observe carbon (a very important elements in urban particulate smog), one should not use a substrate containing carbon. In fact, for best sensitivity, the substrate should consist of elements lighter than carbon. While this is not an absolute requirement, it greatly improves sensitivity. Hence, beryllium substrate which, for 0.5 mil thicknesses, costs about $1.00/sample. If one has heavy loadings, it is possible to subtract a carbon-containing substrate from the sample, but this does

not result in very good sensitivity.

If one can ignore carbon and oxygen, one can get good values for B, N, F, and Na, from mylar substrates, and in fact, the same sample can be run in both system simultaneously.

Figure 18 shows a spectrum taken from a mylar blank, while Figure 19 shows a smog sample impacted on a Be foil. The carbon peak corresponds to about 2 $\mu g/m^3$ of elemental carbon. This work will be accelerated since essentially free beam time is available in tandem operation. It should be also noted that this system is being more and more used in biological studies.
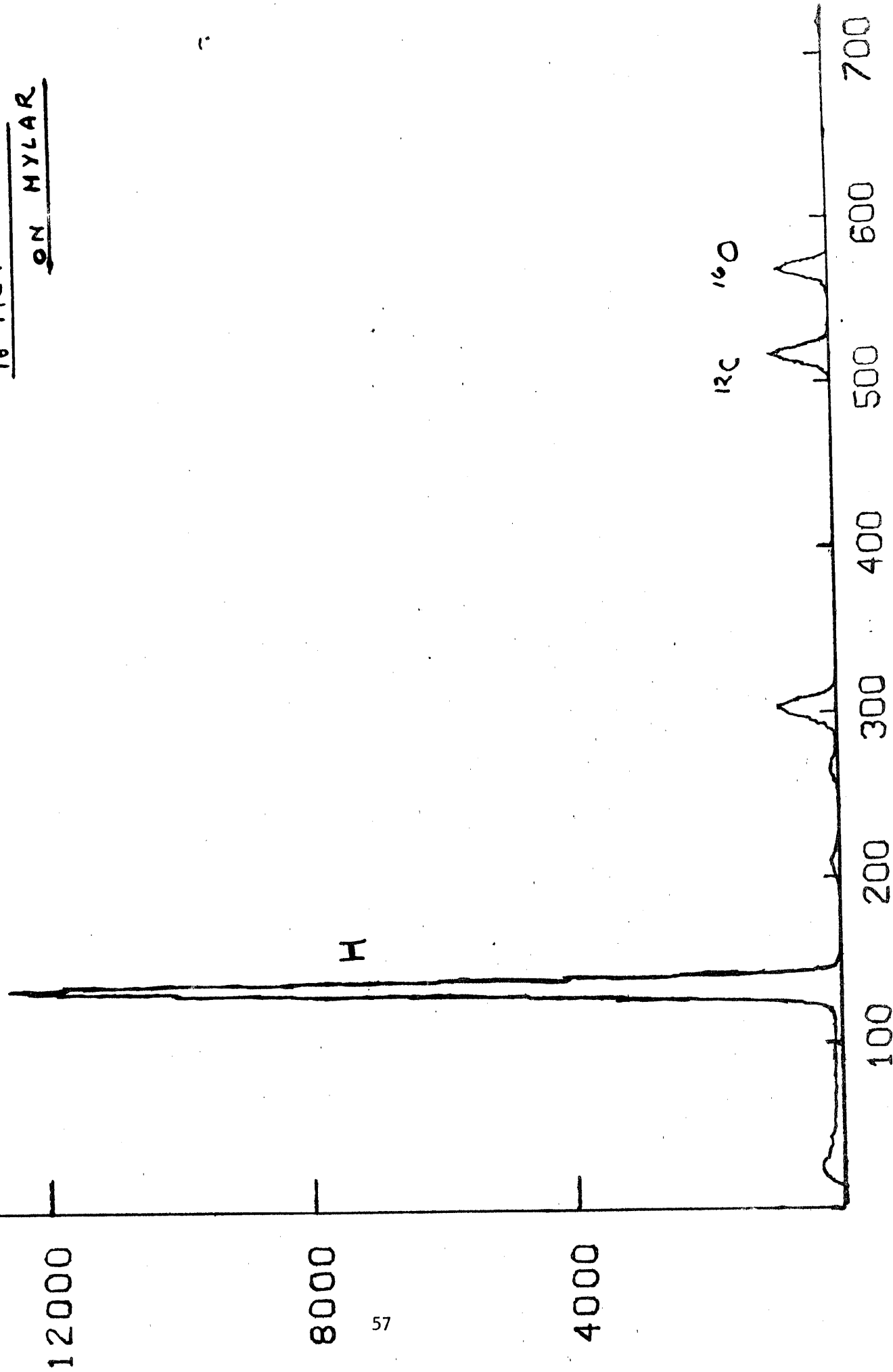
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6. Cost of Analysis

As much as one may hope that the present concern with the environment will turn into increased funding for air quality agencies, one has to be realistic and admit that, especially at the state and local level, abundant new funds will probably not be forthcoming in the near future. Thus, since the utilization of such a system is probably inversely proportional to the cost per unit useful information, a major attempt was made to identify those factors that could be manipulated to reduce the cost of analysis per sample. Very early, it was realized that costs of personnel are usually dominant, and, therfore, an automated system was built that could be operated with a minimum of manpower.

The assumptions made concerning the cost per analysis include one of overriding importance: accelerator beam time can be obtained routinely at a cost of X_1 $/min. This beam time can be obtained in a number of ways:

(1) One could purchase an accelerator dedicated to this type of analysis and amortize it in the charge of X_1 $/min. over some reasonable period of time. This option does not seem viable at this time, if for no other reason than it is not proven that this type of analysis will be
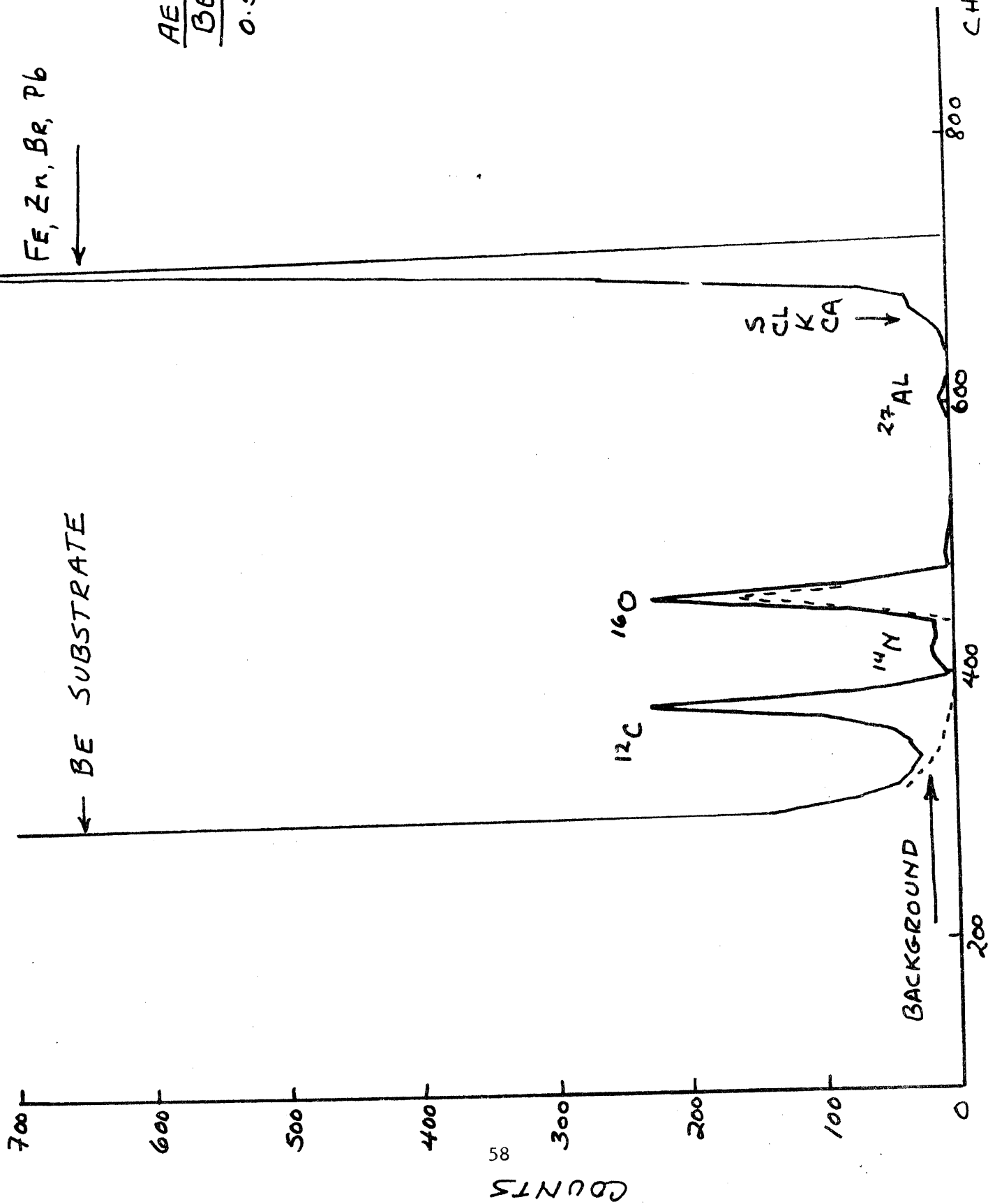
18 MEV α's
on MYLAR

I

^{12}C ^{16}O

100   200   300   400   500   600   700

12000

8000

4000

57

UC DAVIS 10/72

AEROSOL ON
BE – 0.5 → 2μ

BE SUBSTRATE

Fe, Zn, Br, Pb

S
CL
K
CA

^{27}AL

^{16}O

^{14}N

^{12}C

BACKGROUND

CHANNEL #

COUNTS

58

heavily used by air quality agencies. If this were to be the case,
however, and assuming that—

        (a)   this analysis would be used for a minimum of five years,

        (b)   fifty remote stations would be serviced by the system, each
                 generating three samples/day, and

        (c)   the cost of the complete system including the accelerator
                 (a 4 MeV va de Graaf) but excluding the cost of a computer
            (available off line at a cost of $250/hr) is $300,000.–

then the cost of amortizing the system cost (including interest) would
be about $1.25/sample. The key assumption is, of course, a large demand
for such an analysis. Please note that no operating costs are included
in this estimate.

       (2) A second possibility would be to purchase time at some pre-
existing facility, either at a research laboratory or at the growing
number of accelerators becoming associated with hospitals or private
companies for medical isotope production. This option would, in general,
result in a lower cost/sample for system amortization, since shared use
splits this cost among several users. It should be noted that, at a number
of research laboratories, accelerators have been fully amortized and/or
written off the books. Until a major demand is proven, and existing facil-
ities saturate, this option seems to be the least expensive. Conversion
of an existing accelerator to this type of analysis would cost about
$28,000, broken down as follows: (all figures approximate)

Detector and electronics	$9,000.
Target handling systems	$2,000.
Cabling, control wiring	$1,000.
Beam pulsing system	$ 500.
Alpha detectors for light elements	$ 500.
Associated electronics	$2,000.
Beam plumbing and valves	$1,300.
Multichann Analyzer	$4,000.
Magnetic tape and interfacing	$8,000.
	$28,300.

Note that most of this equipment is routinely available in research laboratories.

Once we assume that beam time is available at X,$/min., then one can calculate the cost of analysis per sample in either of two ways:

(1) Figure all costs involved in each analysis, including labor, under the assumption that personnel is available that can work part time in such work. This avoids the necessity of guessing very accurately the total number of samples that must be handled in a year.

(2) Estimate the total load and assume that personnel must be supported totally be this work. This results in a value that is strongly dependent upon the estimated utilization.

We will use the first method, since this fits in rather well with the assumption of shared utilization of the facility, and because this is the method being used at Davis. We thus have gained considerable experience in this type of handling.

Assume that:

Each analysis run takes T_1 min. and includes N_1 samples.

Beam preparation takes T_2 min.

These are charged at the beam time costs of X_1 $/min, so that this cost is

$$C_1 = X_1 (T_1 + T_2) \; \$$$

Pre-run preparation takes T_3 min. by a highly trained technician and post-run wrap-up takes T_4 min. by the same type of person. They are charged at the cost of X_2 $/min., resulting in a cost-

$$C_2 = X_2 (T_1 + T_3 + T_4) \; \$$$

Assuming that N_1 samples are analyzed in Time T_1 min., this gives a partial cost per sample:

$$r_p = (C_1 + C_2)/N_1$$

A number of costs are dependent totally upon the number of samples, so that these costs naturally appear in terms of a fixed cost/sample, r_F.

60

These costs include the slide holders, trays, and substrates (if necessary), labor to mount them, catalog them, handle and record the output data, including magnetic tapes, off-line computation, paper for the line printer, hard copy paper, and costs of amortizing and repairing the components of the analysis system. The total costs will then be:

$$r_T = r_F + r_p$$

As an example of the above calculation, we can consider the case at Davis.

If a sensitivity of 10 ng/cm^2 is used as a target value, this can be achieved in 40 seconds for elements around iron on thin plastic substrates. Then the parameters are (for one eight hour run per week):

$$
\begin{aligned}
\text{for } T_1 &= 8 \text{ hrs.} = 480 \text{ minutes} \\
T_2 &= 1/2 \text{ hr.} = 30 \text{ minutes} \\
T_3 &= 2 \text{ hrs.} = 120 \text{ minutes} \\
T_4 &= 4 \text{ hrs.} = 240 \text{ minutes} \\
X_1 &= \$81/\text{hr. or } \$1.35/\text{min.} \\
X_2 &= \$6 /\text{hr.} = \$0.10/\text{min.}
\end{aligned}
$$

To find the number of samples that can be run in this time, N_1, add to the 40 sec./sample the time to change from sample to sample, load trays, pump down the system, and start again. This is about 20 sec./sample. Thus, 480 samples can be run in eight hours of run time at this sensitivity.

The variable (sensitivity-dependent) cost is then:

$$r_p = \$1.60/\text{sample}$$

Fixed costs (mostly labor) add about $0.50 per sample, so that the net cost under these assumptions is about $2.10 per sample, if no other use is made of the beam. In practice, the beam is designed to be re-used for light element analysis and x-ray analysis to higher sensitivity, and putting a charge of about $20/hr., for each of these five uses almost pays for the beam time by itself. The details of how such calculations work out in the long term depend too strongly on the level of utilization of the system to warrant further comment at this time. These calculations do show, however, that accelerator and system-related costs are not overwhelming in certain situations, and that the final cost for an analysis can be most attractive for many applications.

TABLE 10

Accelerators Capable of 3 MeV/amu $\leq E_i \leq$ 8 MeV/amu

| | Van de Graaffs | | | |
	Single	Tandem + 3-stage	Cyclotrons	Total
National Labs	9	8	4	21
Universities	30	* 24	13	67
				88

* This list does not include accelerators located in hospitals,
private industry, or in countries other than the United States.

IV. THE ROLE OF SUCH SYSTEMS IN AEROSOL ANALYSIS

The system described above was designed under the assumption the
least expensive method for performing elemental analyses of large
numbers of smog samples that was—

> adequately sensitive,
>
> quantitative, and
>
> with broad elemental coverage,

which would probably be the most useful for air quality purposes. The
logic that favored the use of energetic ions was that light elements
(Na → Ca) had to be detected as well as heavier elements. Quantitative
analysis of light elements by x-rays demanded that loadings be kept very
light or matrix effects could introduce major uncertainties. Light load-
ings demand abundant excitation, which requirement was well filled by
accelerator beams.

The use of an accelerator immediately posed certain problems, the
most important of which involved a distinct lack of portability, obtain-
ing access to a facility, shared use of the beam that limits normal
turn-around time to about one week, costs associated with the purchase
of beam time, and possible sample damage under irradiation. While
portability could not be improved, access was assured by the administra-
tion of the Crocker Nuclear Laboratory; turn-around time could be reduced
to a few hours under emergency conditions, costs could be held low through
use of fast, automated system, and sample damage can be held to reasonable
limits on most samples through techniques described above. Once these
major problems have been handled, the advantages of shared use of an
accelerator start to make themselves felt. One is making use of a great
deal of capital; accelerators, electronic systems, computer, etc., that
has been already provided through largely federal sources for other pur-
poses, which tend to keep costs low. One has a large and highly trained
staff available to work on a part-time basis. One can make use of the
beam to look at very light elements, H → F, by alpha scattering, at the
same time one is using the system for heavier elements. Since most of
the mass of the smog aerosol is in this region, this is a useful feature.
The fast analysis necessary to keep costs low results in an extremely

large capacity for doing elemental analyses, and one that can expand to the load without requiring major additional capital investment.

Now that the system exists, certain options open up for air quality agencies in California and elsewhere. One can envisage a proliferation of simple, inexpensive, reliable aerosol sampling units placed around the state, with highest densities in problem areas. These units could collect samples continuously, 24 hrs/day and 365 days/year, in super-respirable, respirable, and subrespirable size ranges, to be analyzed for elemental content every two weeks or so. The information provided on the levels of particulate pollution experienced by the population at large would be extensive. The costs of establishing such a network might look like:

TABLE 11

Costs Associated with a 60-Station Network

	Capital Costs	Operating Costs
Establishment of a Central Analysis Facility* (assuming shared use)	$28,000.	Supported by sample charges
Remote Stations (at $1000 @ + parts, spares)	$75,000.	$25,000.
Analysis of Samples (at $1.50 for foils, $5 for filters)		
Respirable fraction only	—	$33,000.
All size ranges	—	$176,000.
Data Compaction and Reduction to useful forms	$10,000.	$15,000.
	$113,000.	$73,000. to $216,000.

*Already accomplished at Davis.

One essential problem remains that cannot be handled by an off-line system- namely, response to local acute smog episodes. For this purpose, there should be a unit located in or close to the area subject to the acute particulate problem. This unit has to have reasonable support in terms of on-site staff and, hopefully, computational facilities. Use of x-ray fluorescence is highly desirable in this case due to its broad range capabilities, reasonably low capital costs, and fast turn-around time. Several such units could be located around the state, and estimating a cost per unit of $35,000., the net capital cost might be about $105,000. These stations probably would not be as inexpensive on a cost/sample basis as a central facility and would have a more limited throughput capability if one demanded analysis of all components of the smog. They could be extremely useful for studies of limited numbers of elements, however, and could provide an analytical base for local source studies.

Once the desirability of a central analysis laboratory so designed as to minimize costs has been established, the question can be asked as to whether such a facility could be established without the use of an accelerator. My feeling is that this question can be answered in the affirmative, through use of x-ray fluorescence, once it has been established that the technique can obtain quantitative information on light elements at reasonable cost. The light loadings encountered, the problems of certain filter media (Table 8), and the impossibility of seeing all elements at one time as is done by ion-excited x-ray analysis, tend to raise the cost of analysis, however. Probably two and possibly more quasi-monochromatic exciting lines will be necessary to get good elemental coverage. The problems associated with simultaneous multi-line excitation have to be balanced against the additional cost of two separate systems with different exciting lines.

Assuming that these problems can be solved, we can estimate approximately the costs involved in such an analysis. Using two separate exciting systems, and depending on off-line computation, one can estimate a capital cost of about $70,000. Assuming that 15 minutes is required per analysis, and assuming 6 day week, 24 hour/day operation with 8 hours for maintenance/ repair, one can handle about 27,000 samples/year. Assuming that one can do this using two 1/2-time personnel, and that one uses maintenance contracts

or additional personnel to provide major maintenance, one can estimate a personnel cost (at 50% overhead) of about $24,000. This is about $1.00/sample. Cost of system amortization, off-line data reduction, supplies and expenses, secretarial help, etc. will probably raise this to perhaps $2.00 per sample or so. I hope that better figures will be available fairly soon, but in any case, such costs are similar to the present estimate of $1.50/sample used at Davis for routine monitoring purposes. (Note that many of the above costs are included in the beam time including amortization of all degradable items in the laboratory).

The optimum strategy for California in the long term is not yet clear, but certain points can be proposed at this time.

(1) The cost of total elemental analysis of an atmospheric particulate sample has dropped from a few hundred dollars to a few dollars in the past year.

(2) The use of a capital-intensive, fully amortized system such as the Crocker Nuclear Laboratory has allowed such costs to be attained for extremely small additional capital investment by the State of California.

(3) The resulting UCD-ARB system can maintain such costs (and reduce them further) for almost any number of samples per year, from the present limit of about 250,000 to well over 1,000,000.

(4) Based upon the low cost of analysis obtainable by the UCD-ARB aerosol analysis system, it is now both feasible and desirable to proliferate inexpense monitoring units designed to sample at least the respirable fraction of the smog aerosol on a continuous basis (24 hrs/day, 365 days/year) throughout critical areas in the state.

(5) It is also possible to vastly expand personal aerosol monitoring for hazardous occupations. The same low costs/sample can be applied to properly designed personal monitors.

(6) Construction of an x-ray fluorescence-based system to handle the throughputs that will be generated by planned monitoring activities would be expensive. Such a facility should not be built lacking

clear evidence that more or better information per monitoring dollar could be obtained by it than by the present ion-excited system.

(7) Construction of a limited number of transportable, x-ray excited aerosol collection and analysis systems should be accomplished to allow fast response to acute smog episodes and to allow continuing studies of aerosol sources.

Acknowledgements

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   Dr. Glen Gordon's study of Boston using neutron activation analysis (now at the University of Maryland).
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